

CONFORMATIONAL PROPERTIES OF POLYMERS

By

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CONFORMATIONAL PROPERTIES OF POLYMERS

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In this thesis, I study the conformational properties of polymers in a stationary and stationary states.

In the first part of my thesis, I study the conformations of polymers in a stationary state. I consider two cases: (1) the motion of a polymer penetrating a membrane and (2) the dynamics of DNA molecules in a gel. In the first case, I assume that a polymer crosses a membrane several times during the process of penetration. The polymer reptates along its own contour. The mobility of the polymer chain is related to its configuration which are characterized by the number of crossings with the membrane. I find the configurations which give the main contribution to the transport and calculate the overall permeability in the case of both Zimm and Rouse dynamics. As a second system, I consider the motion of a long DNA molecule confined in a gel. When a strong electric

field is applied, the electric field forces the DNA into a two-side structure. The dynamics of large segments of DNA is almost deterministic and can be described by a set of simple mechanical equations. This allows the numerical study of gel electrophoresis of DNA. I confirm the hypothesis of the statistical self-similarity of a moving polymer.

In the second part of the thesis, there are three major sections all dealing with configurational properties of a single isolated charged polymer. 1) I study the configurational statistics of a ring polyelectrolyte chain. In addition to the random like transitions similar to that in a linear chain, I found that a ring polyelectrolyte has a metastable phase where the configurations are restricted by the randomness in the charge distribution. 2) I study new exact solutions of the nonlinear Poisson-Boltzmann equation describing counterion condensation on a strongly charged polymer in the dilute regime. The condensation has to be brought from three-dimensional space and the entropy loss is $3/2$ times larger than in the picture of Manning. The condensation occurs at a critical line charge density $\lambda = 3/2$, which is $3/2$ times larger than in Manning's theory. 3) I study the rigidity of the charged polymer in the presence of counterion condensation. I show that the condensation of counterions changes the local structure of the charged polymer more than in the Debye-Hückel approximation. By solving the Poisson-Boltzmann equation in cylindrical coordinates in the vicinity of charged polymer, I show that the persistence length l_p of a strongly charged polymer is proportional to the Debye radius $l_D \sim R_D$.

CHAPTER 1

INTRODUCTION

A polymer is a macromolecule consisting of many repetitions of the same basic unit called "monomer" [1-4]. For example, polyethylene is the polymer made of ethylene molecules (monomers). A DNA molecule consists of up to 10^7 nucleotides. Polymers are very common in our life. Plastics, rubbers, proteins and other biomolecules are polymers. A material made of long molecules has very different properties from one made of small molecules. Polymeric materials are very flexible and viscous and elastic. However, because of their complexity, polymers have been studied only for a few decades.

The macromolecule of a polymer in solution depends on the solvent, concentration, and temperature. In a good solvent, the interactions between monomers and solvent are attractive, therefore, polymers can dissolve. The effective interactions between monomers are repulsive so that polymers stretch out. On the other hand, in poor solvents, the net interactions between monomers is attractive; therefore, precipitation occurs. Depending on the concentration, a polymer solution can again be classified into three different regions: dilute, semi-dilute and concentrated solutions.

Experimentally, in order to characterize the polymer (for example, to measure the molecular weight), one places the isolated polymer in a dilute solution where the interactions with other polymer chains are negligible.

However, a typical polymer material is rubber like and many polymers are entangled with each other. In order to understand the properties of polymeric materials, we have to consider many chain effects. Polymers are long one dimensional objects and they can not cross each other. In a many chain system, the topological interactions between polymers are important. Topological interactions strongly affect the dynamical properties because they impose topological constraints on the motion of polymers. With new concepts introduced by P. G. de Gennes [1] and E. F. Edwards [2], the framework to understand the many chain systems like concentrated solution and melts, has been established. There are two models of the dynamics of entangled polymers: Rouse and Zimm dynamics. In the Zimm model, the monomers are coupled to each other by hydrodynamic interactions, while the Rouse model assumes that there is no hydrodynamic coupling between different monomers [3, 4].

In the first part of my thesis, I study the conformational properties of polymer in dynamical processes in the presence of topological obstacles. In chapter 2, I study the conformational properties of a polymer penetrating a membrane. There is an interplay between dynamics and conformational properties. The dynamics of the polymer is discussed in both the Rouse and the Zimm regime. In chapter 3, the dynamics of DNA molecules – ultra long polyelectrolytes – in gel electrophoresis is studied. The stretched tube-like structure of the DNA conformation under the strong field electrophoresis provides deterministic equations for their dynamics. Through theoretical analysis and the numerical solution of these coupled differential equations, I calculate the average velocity, the period of

models, the loop-size distribution, the critical velocity of the melting of twisted structures and other properties.

In the second part of my thesis, I study the conformational properties of a single isolated charged polymer. Polymers consisting of monomers which include ionizable groups are called "polyelectrolytes". The Coulomb interaction between the monomers affects the microscopic structure of polymers, which results in very different properties of polyelectrolytes compared to that of neutral polymers. The mean theoretical difficulties arise with the long range nature of the Coulomb interaction.

This part of the thesis (chapters 4 - 7) is organized in the following way. In chapter 4, the general difficulties in dealing with charged polymers are discussed. In chapter 5, I discuss the condensation of a ring polyelectrolyte. The conformation of polyelectrolytes and polyanionopolymers have been studied by Golovyski et al. [6] and Kauter et al. [8,7], respectively. A polyanionopolymer is distinguished from a polyelectrolyte because it carries both positive and negative ions along its backbone. There are similarities between the static configurations of a linear polyanionopolymer and polyelectrolyte. After a short review of these previous works, I discuss the condensation transition phase found in a ring polyanionopolymer chain. I use Monte Carlo simulations in order to illustrate the properties of the condensation. Simple mean field type arguments are presented.

The analytic approach to solve the nonlinear Poisson-Boltzmann equation is illustrated in chapter 6. A new solution of the Poisson-Boltzmann equation in the dilute solution regime provides a new picture of the condensation of monodisperse

I compare the results with the classical coagulation theory [8] suggested by Manning.

In Chapter 5, I analytically study the effect of the nonlinearity of the Poisson-Boltzmann equation on the persistence length of polyelectrolytes.

The results are summarized in the conclusion, and topics for further study are discussed.

CHAPTER 2

DIFFUSION OF A POLYMER THROUGH A THIN MEMBRANE

In a recent paper Voss and Demuth [1] considered an interesting and important problem of diffusion of a linear polymer in the presence of permeable membranes. This type of transport is the key element of many biological and technological processes. It has the potential to be used for the separation of polymers of different lengths [2] and different compositions. It can also be used for controlled drug release. Usually a membrane is thought of as a thin material interface separating two solutions. Such a membrane is a strongly fluctuating object which might have a rich variety of different phases by itself [3,4-10]. The mechanical properties of the membrane might change with the adsorption of a polymer on its surface [11]. Besides it is a mechanically fragile object which can make it difficult to perform well controlled microscopic measurements.

A simple way to avoid this problem is to make a two dimensional "membrane" by putting together two sheets of gel. The surface of the gel can be treated in such a way, that when two sheets of a gel are brought together they form an internal interface. This membrane is mechanically very stable and its permeability can be controlled by various surface treatment techniques.

I consider a dilute solution of polymer chains, each made of N monomers. The length of each monomer is b . The bulk concentration ρ_0 of polymer on one side of the membrane is maintained constant and is zero on the other side.

The polymers are penetrating the membrane which has negligible thickness and a constant α of order 1. The membrane has a chemical potential μ measured with respect to the bulk. The chemical potential will always be given as $k_B T \ln \alpha$. The statistical weight of any polymer configurations with k crossings of the membrane compared with the random configuration in the bulk, has an additional factor $\alpha^{-k\alpha}$ associated with these crossings. I neglect all excluded volume interactions. For dilute solutions I assume that the bulk chemical potential on both sides of the membrane is zero. Later, in order to describe likelihood of concentrated polymer solutions through the membrane I assign different bulk chemical potentials on different sides of the membrane.

Wess and Deutsch [8] considered the simplest case where the chemical potential on the membrane is zero ($\mu = 0$) and assumed that the configurations of the polymer crossing the membrane is Gaussian (see Fig. 3.1.4). In this "typical" configuration the polymer crosses the membrane $\alpha/\sqrt{N}$ times and its mobility is greatly reduced compared to its mobility in the solvent. The configurations with these crossings are thermodynamically unfavorable, but they have large mobility. I will show below that if effects of hydrodynamic friction are taken into account, these configurations give the dominant contribution to the total transport through the membrane. The chemical potential of the membrane acts as an additional control parameter in this problem. If μ is positive (negative) it will result in an decrease (increase) of the number of crossings k and affect the transport through the membrane.

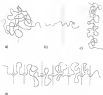


Figure 7.1: Configurations of the polymer during penetration of a monolayer of Gaussian configurations. The number of crossings k in the typical configuration is $k \sim N^{1/2}$. (b), (c): Sketch of a typical configuration, when $\mu > 0$ and $\mu < 0$. The number of crossings k is controlled by the chemical potential μ . (c): Effective tube picture. The motion of a polymer can be thought of as a reptation through a series of "gates". The distance between the gates is of order $k(N)^{1/2}$.

3.1. Reptation Time

The mobility of a polymer which crosses the membrane k times (see Fig. 2.1 *d*) can be calculated following the analogy with reptation in a tube (3, 14, 15). The typical length of a polymer between the two subsequent crossings of a membrane is N/k , and the physical distance between the crossing points is $l = \sqrt{N/k}$ (see Fig. 2.1 *d*). The diffusion time through the membrane can be calculated as the time needed to reptate through k "gates", each a distance $l = \sqrt{N/k}$ apart from each other. The total length of this hypothetical tube is $L = l \cdot \sqrt{N}$ and the time needed for a polymer to reptate through the tube is $t = L^2/D = l^2 N^2/D$. Here, D is the diffusion coefficient of a polymer.

The simplest approximation for D is given by the Rouse model for mobility with $D = D_0/N$ and reptation time $\tau_r^0 = l^2 N^2/D_0$. For a Gaussian configuration with $k = \sqrt{N}$ this will reproduce the Tazuke and Okazaki (5) result $t \sim N^{3/2}$.

The application of Rouse dynamics can be justified in special cases when the hydrodynamic interactions between monomers of the chain can be neglected. This can happen due to the presence of other polymers (crowded solution), or if the polymer is confined inside the gel which damps the hydrodynamic interaction between monomers of the chain. In the latter case, the membrane is actually an interface between two pieces of a gel brought together as described before.

If hydrodynamic effects are important, the diffusion coefficient is controlled by viscous friction at the gates where the polymer penetrates through the membrane as shown in Fig. 2.2. In order to calculate the friction I assume that the polymer is pulled with a small velocity V through the gate. This velocity should be small



FIGURE 2.1

Figure 2.1. Illustration for the calculation of hydrodynamic friction. The polymer is pulled through the gate with small velocity V . The friction on a polymer segment of length N , is about the same as that of a sphere with radius $R_s = (3N^2/4)^{1/2}$ moving with a drag velocity of $V_s = R_s V / N = 1/2 V$. Most of the dissipation of energy occurs at a maximum scale $\sim a$ (gate size). The contribution from large scales is negligible.

enough to treat the configurations of the polymer as if it were in equilibrium. The friction on each section of a polymer of length N_1 (as revealed from the gate) and size $R_1 = \sqrt{N_1}a$ can be calculated as the viscous friction of a sphere of radius R_1 pulled with velocity $V_1 = R_1 N_1 / N_1$ towards the gate. The friction is $f = 6\pi\eta R_1 V_1$ (η is solvent viscosity). The rate of energy dissipation due to this friction is $P = f V_1 \sim 1/\lambda_1$. This means that the main contribution to friction comes from the subchain with R_1 which is the gate size λ .

If there is no large dispersion in the sizes of different gates, the dissipation of energy at each gate is about the same and the total dissipation is proportional to the number of gates i . The overall mobility of the polymer is $\sim 1/\lambda$ and the diffusion coefficient can be calculated from the Einstein relation between mobility and diffusion: $D = k_B T \mu$. The relaxation time in this case is $\tau_1^E = P N^2 a^2 / D$. Here D_0 is defined in terms of solvent viscosity η : $D_0 = k_B T^2 / \eta$. I will use this because of the N^2 dependence of the relaxation time τ_1^E the contribution to the transport from configurations which cross the membrane many times is suppressed, and configurations with few crossings give the main contribution to the membrane transport. Below, I will use the superscripts R and E in order to distinguish between referring to Rouse and Einstein dynamics.

2.3 Configurations of Polymers at the Membrane - Channels

The concentration of polymers density at the membrane is an important parameter in my problem it depends on bulk concentration (ρ , and θ) on both sides of the membrane and on the chemical potential of the membrane μ_m in

shown in Appendix A that the concentration is nearly one half of the equilibrium concentration ρ_0 , which would be established on the membrane when the bulk concentration on both sides of the membrane is ρ_0 .

$$\rho_0 = \frac{1}{2} C_0 b_0 \quad (2.14)$$

The polymers at the membrane have different mobility depending on the configuration of these polymers. I will consider the flow Π through the membrane as a sum over contributions from different channels: $\Pi = \sum \Pi_k$. Each channel, with index k describes the motion of polymers which cross the membrane k times. The density of polymers in the k th channel is ρ_k and $\sum \rho_k = \rho_0$. The polymer density ρ_k on each side of the gel can be related to the density in the equilibrium problem,

$$\rho_k = \frac{1}{2} C_k b_k \quad (2.15)$$

The surface density of these polymers (density per unit area of the membrane) can be obtained by multiplying ρ_k by the thickness of the layer of polymers $R_k = z\sqrt{B}$ (see Fig. 2.1 a). In every time interval t_k^0 (or t_k^1) the polymer in the channel k are removed; other polymers leave the channel, other polymers move in. The contribution of each channel to the transport per unit area of the membrane is

$$\Pi_k = \frac{R_k}{t_k} \rho_k \quad (2.16)$$

where t_k is either the Brown (t_k^0) or Zimm (t_k^1) relaxation time. Π_k has the dimension of number of polymers/unit area $\times$ sec⁻¹. The total transport through

the modulus measured in $(\mu_0 D_0 / kT)$ units is

$$\bar{M}^2 = N^{-1} \bar{\langle 1/k \rangle}, \quad \bar{M}^2 = N^{-1} \bar{\langle 1/k^2 \rangle} \quad (11-4)$$

where $\langle 1/k \rangle$, $\langle 1/k^2 \rangle$ are properly weighted average moments of k

$$\langle 1/k \rangle = \sum \frac{dk}{k} \frac{1}{k}, \quad \langle 1/k^2 \rangle = \sum \frac{dk}{k} \frac{1}{k^2} \quad (11-5)$$

(The mass transfer formula can be obtained by multiplying $\bar{M}_0$ by the index of the polymerization N .)

1.3 Calculation of Average Moments of k

The average in Eq. 11-3 can be done exactly with the use of the equilibrium density distribution (see Eqs. 1-1 and 1-2). At any particular value of the mean bond potential μ , the partition function of the chain is the sum of the partition functions with different numbers of crosslinks k ,

$$Z = \sum_k Z_k = \sum_k Z_k^0 e^{-\mu k} \quad (11-6)$$

Each particular Z_k can be factored into the product of two terms, Z_k^0 and $e^{-\mu k}$, where Z_k^0 is the partition function at $\mu = 0$ and the relative weight $e^{-\mu k}$ contains all dependence on the chemical potential. The sum in Eq. 11-6 which

given $\langle 1/k \rangle$ can be obtained by integrating Eq. 3.4

$$\langle 1/k \rangle = \frac{1}{Z} \sum_k \frac{1}{k} Z_k e^{-\mu} = \frac{1}{Z} \int_0^\infty Z(k) dk e^{-\mu} \quad (3.7)$$

The case in Eq. 3.4 which gives $\langle 1/k^2 \rangle$ can be obtained by double integration

$$\langle 1/k^2 \rangle = \frac{1}{Z} \sum_k \frac{1}{k^2} Z_k e^{-\mu} = \frac{1}{Z} \int_0^\infty \int_0^\infty Z(k, k') dk' dk e^{-\mu} \quad (3.8)$$

The detailed calculation of the partition function $Z[\mu, N]$ is given in Appendix B. This calculation is made in a way similar to the calculation of the partition function in the adsorption problem [10, 11]. I find

$$Z[\mu, N] = e^{-N\mu} e^{-\mu^2 N^2/4} \int_0^\infty dx e^{-\mu x} \int_0^\infty dy e^{-\mu y} \sqrt{xy} \quad (3.9)$$

with $Z^0(N) = 1$. Equations 3.3, 3.7, 3.8 give a closed form description of the flow through the membrane. The results for various limiting cases can be obtained knowing that the partition function $Z[\mu, N]$ is a universal function of $\zeta = \sqrt{\mu^2 N^2/4}$ with an additional factor $e^{-\mu}$. This factor means that my configuration has at least one crossing of the membrane. For $\zeta \gg 1$, $Z[\mu, N]$ has an asymptotic form $\sim \mu^{-1/2} N^{1/2}$. Integrating that function I obtain

$$\langle 1/k \rangle = \frac{1}{\mu} \quad \langle 1/k^2 \rangle = -\log(\mu) \quad (3.10)$$

(and $\langle 1/k \rangle = \sqrt{N} \ll 1/k^2 \rangle = -\log(N)$ at small $\mu < 1/\sqrt{N}$.)

1.4 Configurational Dynamics

1.4.1 Revised Monomers ($\mu = 0$)

The configurations which contain the monomers only seen (shown in the Fig. 1.1 b) has small statistical weight, each half of the chain to the right and left of the monomers can be thought of as a $n = N/2$ step random walk, which means on the monomers and does not cross the monomers again. The probability of such a random walk is of order $1/\sqrt{N}$ (see Eq. B.4 in Appendix B). The statistical weight of a configuration with two such random walks is $\sim 1/N$.

The average number of crossings k in the typical configurations of a polymer chain is of order of $\sqrt{N}$. It is shown in Appendix B that the relative weight of configurations with k crossings is $\sim k/N$. In the case of Rouse dynamics it happens that all $\sqrt{N}$ chains give the same contribution to the total transport ($\Omega_k^R \sim N^{-1/2}$) and the total transport is ($\rho_{\text{Rouse}} \sim \sqrt{N}$)

$$\Omega^R = \sum_{k=0}^{\sqrt{N}} \Omega_k^R \sim N^{-1/2} \quad (1.11)$$

For Rouse dynamics chains with small k give contributions proportional to $1/k$ ($\Omega_k^R \sim k^{-1}N^{-1/2}$). Integrating over all k gives the logarithmic N dependence of Ω

$$\Omega^R \sim \frac{1}{2}N^{-1/2} \log N \quad (2.12)$$

2.4.2 Repulsive Monomers ($\mu > 0$)

In this case there is a factor $e^{-\beta\mu}$ on each Π_i . If $\mu < 1/\sqrt{N}$, this factor does not affect configurations statistically. If $\mu > 1/\sqrt{N}$, it will produce an effective cut-off in the summation over i in Eq. 2.15. The maximal number of crossings is in of order of $i \sim 1/\mu$. At $\mu > 1$ only configurations with one crossing (see Fig. 3.1 b) are relevant. For the Rouse model, the main effect of monomers potential is to controlling the number of chains contributing to the transport. For Zimm dynamics the main contribution comes from small i . Instead of Eqs. 2.21 and 2.22 we have

$$\Xi^D \sim \mu^{-1} N^{1.5}, \quad \Gamma^D \sim N^{1.5} \log\left(\frac{N}{\mu}\right) \quad (2.23)$$

At $\mu > 1$ there is a crossover in both formulas to the single chain regime

$$\Xi^D \sim \mu^{-1.5}, \quad \Gamma^D \sim N^{1.5} \quad (2.24)$$

2.4.3 Attractive Monomers ($\mu < 0$)

At $|\mu| > 1/\sqrt{N}$ a polymer is adsorbed on the monomers. The typical polymer configurations can be considered as a chain of "adsorption blobs," each blob consisting of $N_b = 1/\mu^2$ monomers. On the scale less than the blob size the chain has the same statistics as a random walk and crosses the monomers $b_p = 1/|\mu|$ times, so that the adsorption energy of a blob is of order one (in $k_B T$ units). The average number of monomers crossings is proportional to the length of a

polymer

$$\bar{I} = (N/N_p) \bar{I}_p = (n/2) \quad (2.15)$$

The factor r^{2k} increases the relative weight of configurations with large k . The main contribution to the transport comes from about $1/2n$ channels with k in $\bar{I}$

$$\Gamma^2 = \frac{r^{2\bar{I}}}{\sum_k r^{2k}} \quad (2.16)$$

In the case of Zimm dynamics there are two main contributions to the transport, one from small k (dis-soluted) configurations and the other from large k (ad-sorbed) configurations at higher μ . The total transport is the sum of these two contributions $\bar{I}^2 = \bar{I}_1^2 + \bar{I}_2^2$

$$\bar{I}_1^2 = \frac{r^{2k_0} \log n}{N+1} \quad (\text{small } k), \quad \bar{I}_2^2 = \frac{r^{2\bar{I}}}{\sum_k r^{2k}} \quad (\text{large } k) \quad (2.17)$$

When $r^{2k_0}/(N_p(N+1)) \approx 1/2n$, $r^{2\bar{I}}/(N_p^2 N^{4/3}) \approx 1/2n$, the overall permeability of the membrane becomes comparable with the permeability of the solvent $N^{-1/3}$. In this regime, the membrane is transparent. This effect can only be observed in the limit of very low bulk concentration of polymer ρ . The concentration of polymer on the membrane $= r^{2\bar{I}}$ decreases faster than ρ , and should still be less than the concentration at which interactions between polymers become important. Otherwise the effects of association of polymers will cancel the access to the membrane and the flow through the membrane will be saturated or even stopped.

3.4.4 Filtration of a Coarsened Solution.

The effects of excluded volume interactions are not considered in our discussion, but it seems likely approximating these effects can be easily incorporated in our description, by assuming that there are two different chemical potentials on both sides of the membrane, $\mu_1 > \mu_2$. The difference of chemical potentials is proportional to the difference in monomer concentrations, $\mu_1/\bar{R}$ and $\mu_2/\bar{R}$ on both sides of the membrane:

$$\mu_1 - \mu_2 = (\mu_1 - \mu_2)N\bar{R} = \Delta\mu N\bar{R} \quad (3.18)$$

where $\bar{R}$ is the second virial coefficient.

In this case there is a difference of the osmotic pressure on both sides of the membrane. This results in a force on the monomers when they cross the membrane. The force is directed towards the dilute phase and produces an average drag velocity

$$v^{\text{os}} = D_p \Delta\mu \bar{R} \quad v^{\text{tr}} = D_p \Delta\mu \bar{R} \bar{R} / \zeta \quad (3.19)$$

If the time ζ_{app} a polymer needs to cross the membrane is shorter than the diffusion time $\tau^{\text{tr}}(R^2)$, the transport $\Pi = \mu_1/\bar{R}_1 - \mu_2/\bar{R}_2$ is nonlinear. This happens under the condition that

$$N^{\text{tr}}(\zeta_{\text{app}}) < 1. \quad (3.20)$$

The configurations with multiple crossings of the membrane are suppressed as this requires because of the low probability of return to the dense phase.

2.1. Introduction

I considered a problem of a polymer chain penetrating through a porous membrane by calculating probabilities of different configurations of a polymer and the corresponding velocities. I found the optimal configurations which give the main contribution to the transport through the membrane. In case of Rouse dynamics when $\mu = 2$ the configurations with different numbers of monomers crossing it give equal contribution. At nonzero μ these contributions are proportional to $n^{-\mu/2}$, which give preference to configurations with small (large) k for a repulsive (attractive) membrane.

If hydrodynamic interactions are important, the main friction effects during the motion of a polymer are localized at the points where the polymer crosses the membrane. In this case, the main contribution to the transport comes from configurations with small numbers of k . If the membrane is attractive, the main contribution is shifted to configurations with large k .

The process of diffusion through the membrane can be used for separation of polymers with different lengths. The effectiveness of this process can be characterized by the $N^{-\mu}$ dependence in the expression for the transport Eqs. 2.11-2.14. The exponent μ varies from 0.5 to 2.5. There is also an additional exponential dependence on N in Eqs. 2.11 and 14 for the attractive membrane. The use of selective membranes ($\mu < 0$) might not be very practical because of low permeability and the possibility of changing membrane properties by adsorbed polymer.

CHAPTER 3 DETERMINISTIC MODEL OF DNA GEL ELECTROPHORESIS IN A STRONG ELECTRIC FIELD

3.1 Reptation Tube Model

The motion of a high molecular weight polymer in a gel is constrained by the strands of the gel. The strands limit the displacement of a polymer in the direction transverse to its contour. In the tube model, these topological constraints of network strands are replaced by a confining tube [26,29] (of diameter similar to the size of the pores). In the absence of an external field, the chain moves through a gel along this tube by a reptation mechanism [1,2]. The presence of an electric field introduces a bias in the motion of charged polymer. The thermally activated motion along the tube in the field direction is more probable than in the opposite direction. The reptation with a bias is the dominant mechanism of polymer motion in relatively weak fields [20-22]. This model works remarkably well for the intermediate regime even at large fields [27]. As the electric field E becomes stronger, the chain can no longer move exclusively along its confinement (tube). If the electric energy of the charged rearrangement strand is comparable to the thermal energy $k_B T$

$$q\Phi_0 \approx k_B T \quad (3.1)$$

the walls of the tube are no longer able to conduct the polymer. Here q is the charge per "blob." (The section of the chain contained in one pore of size a is called a "blob".)

The external field can pull double folded loops of the molecule through the gaps between the gel fibers [31]. The strands of the chain link out of the tube as the loops of blobs under the influence of the field. These loops have been found both in computer simulations [31-33] and by direct observation of individual, fluorescently stained DNA molecules under the microscope [34-36]. There is no indication that the average number of loops increases with molecular weight.

A remarkable feature of the structure of a moving polymer was found in the computer simulations by Dele and Flory [37-39] and by Doering [40]. The results of these simulations indicate that the motion of an ultra-high molecular weight polymer is qualitatively different from the "hang and slip" mechanism of motion of a lower molecular weight polymer.

In this chapter, I present results for the recently proposed "deterministic model" [41] of DNA motion through a gel in a strong electric field. I discuss detailed information about the statistical properties of loops and tail over threshold fractions in their dynamics. The model is almost deterministic and allows the study of DNA electrophoresis for molecular weights unattainable in usual simulations. In the next section, I describe the deterministic model of gel electrophoresis. In section 3.2, the analytical predictions for this model will be presented. In section 3.3, I give the results of my computer simulation. In the last section of

this chapter. I summarize the main results and discuss the limitations of the deterministic model.

3.1. Deterministic Model

A schematic sketch of a typical configuration of a growing linear polymer with many loops (branches) is shown in Fig. 3.1. It is an oversimplified sketch, and the displacements perpendicular to the electric field are considered unimportant and are not shown to scale. The typical configuration consists of a hierarchy of branches of various sizes. The polymer is fully stretched everywhere except near the tips of the branches where the branch tension is zero [20]. I assume that at the tips of the branches the RSCl_2 is in the end like equilibration, with a small amount of stored length that is negligible in my simulations. Branch mergers is a tug of war with each other and those that are closer to the field grow at the expense of the others [20]. While these branches grow, their tips eventually stretch to the gel and might split, creating new branches. Some of these small branches grow, while others disappear.

The motion of the large sections of the chain (for example section AB of Fig. 3.1) can be described by simple deterministic equations. The tension at the branch tips is zero. This implies that instantaneously there is no mechanical force between the strand and the rest of the polymer. This section of the chain is moving because of the asymmetry of the lengths AC and CB . The equation



Figure 3.1. Two line configurations of a linear polymer. The schematic self-number structure of a walking polymer is shown on the right. The sizes of the branches are proportional to their distance from the leading tip (Eq. 3.5). The number of branches is proportional to the logarithm of molecular size.

of motion for that strand is

$$v = \frac{\eta F (L_{AD} - L_{GB})}{\zeta (L_{AD} + L_{GB})} = v_s A_{ADG} \quad (3.2)$$

where ζ is the friction coefficient per chain section of size s and with charge q , $v_s \equiv \eta F/\zeta$ and L_{AD} and L_{GB} are the lengths of strands AD and GB , respectively. The velocity of this segment depends only on the asymmetry factor $A_{ADG} \equiv [L_{AD} - L_{GB}]/(L_{AD} + L_{GB})$ of the two competing strands AD and GB hanging on the common gel strand “back” G . If we know the velocities of each strand it is easy to write the velocity of the slip points

$$\frac{dL_{AD}}{dt} = v_s \frac{1}{2} (A_{ADG} - A_{GBG}), \quad \frac{dL_{GB}}{dt} = v_s \frac{1}{2} (A_{GBG} - A_{ADG}) \quad (3.3)$$

Because of the strong field, the chain is fully stretched most of the time and the total length of the polymer (the sum of lengths of all strands) remains constant. I extended this description to the case when some parts of the polymer are in a free fall. This happens when one of the ends (on the right or left side of Fig. 5.1) is pulled over the (antagonistic) hook by the rest of the chain. I make the assumption that, when this happens, the strand moves with a homogeneous free fall velocity v_f .

Equations 3.1 and 3.3, written for every strand of a polymer chain, form a set of coupled linear differential equations. These equations can be solved numerically. When the length L_i of a strand becomes zero this strand disappears and the set of equations of motion for the adjacent strands is modified. The above



Figure 3.2: The schematic picture of the top splitting. After crossing the point $x = \text{distance}$, the top could split into two with probability p . During this process the total length of the chain does not change.

equations are completely deterministic, but they describe only the evolution of existing branches and their disappearance. The creation of new branches must be added to this model.

I assume that each time a top travels distance x and moves from one point to the neighboring one, there is a probability p that it will hit an obstacle and will split into two (see Fig. 3.2). Two small branches with length l_1 and l_2 are created as a result of the split.

The total length is conserved during this process (see Fig. 3.2)

$$L_1^i = L_1 - l_1, \quad L_{i+1}^i = L_{i+1} - l_2, \quad L_{i+1}^i = l_1, \quad L_{i+1}^i = l_2 \quad (3.4)$$

The initial sizes of new lesions $\{l_i, i_0\}$ are determined randomly in the interval $[0, \frac{L}{2}]$ in units of the persistence λ . This is the only non-deterministic part of my model. After the creation of the new lesions, their dynamics is controlled by Eqs. 3.1 and 3.3.

I study the dynamics of linear and circular polymers with length ranging between 10^2 and $10^4\lambda$, which corresponds to $10^{11} - 10^3$ nucleotides. Everywhere below I will use persistence units (a typical persistence unit is 3000 Å) and omitting approximately 1000 times units, see for example Dele and Yarey [41]. I compare the results for linear and circular polymers in order to isolate and to understand the real effects.

The total number of linear differential equations to be integrated for each time step is twice the number of lesions. This number grows only logarithmically with molecular weight. The evolution time of a DNA configuration is the typical time during which the polymer is displaced along the field by its average size. This time is proportional to the molecular weight of the polymer. Thus, the actual computational time of my simulation grows only as $N \log N$ with the molecular weight N . The evolution for the 1 nucleotide DNA (period length 3000 persistence units) for about 100 evolution times takes a few minutes on a 500M (space 600) (30 MHz CPU speed) workstation.

First, I consider a circular polymer. For a linear polymer the results are basically the same, but with broader statistical distributions.

3.3 Analytical Results

3.3.1 Scaling

In Olickler and Rabenstein [44], it is argued that the average drift velocity is independent of the length of the DNA. It is also explained the origin of the statistical self-similarity of the moving polymer. Both of these properties are due to the fact that the same equations controlling the evolution of a particular configuration are made invariant. The velocity of a particular strand calculated with Eq. 3.3 depends only on the ratio of the geometrical sizes d_{AC}/L_{DS} , but not on their absolute values. I can study the dynamics of some configurations of a polymer of length N using Eqs. 3.3 and 3.5 and then multiply all logarithmic terms, rates and times by an arbitrary factor λ . I obtain the description of the dynamics for the polymer of size λN . The only process which violates this scaling is the stochastic mechanism of the creation of new branches, and I will address this issue in the statistical simulation section. The lifetime of each side branch of a self-similar tree-like structure proposed by Olickler and Rabenstein [44] is proportional to its distance from the leading tip (Fig. 3.1). This is the time during which this branch (that was created in the vicinity of a leading tip) competed with others and survived, while the tip moves forward. When all velocities in the problem are proportional to v_p , the size of the side branch should be of the same order of magnitude as the distance from the leading tip. I expect that on each time scale the number of surviving branches will be the same (of order unity), hence, the total number of branches n is proportional to the logarithm of the total

length R of the DSD,

$$n = \log R \quad (3-5)$$

The probability to find a branch in the size interval $[L, L + dL]$ is

$$P(L) = 1/L \quad (3-6)$$

3.3.3 Critical Velocity

The dynamics of the two-like structure (Fig. 3.1) is intimately related to the process of creation of new branches (buds) and their disappearance. When the tip of a branch splits in two (see Fig. 3-2) the new baby branches are trying to outgrow each other. I assume that the velocities of both branches v_1 and v_2 depend on the large scale details of the configuration and are constant during this process. We also assume that the asymmetry parameter $A = (j_1 - j_2)/(j_1 + j_2)$ of the initial mass j_1, j_2 of new branches is uniformly distributed in the interval $[-1, 1]$. If the velocity of the splitting tip is negligible or zero (v_1 or $v_2 \approx 0$), the time needed for the larger of the two larvae to overweigh the other is very short and is of order $\max\{j_1, j_2\}/v_0$. In the other limit, when the tip is moving with free fall velocity $v_1 = v_2 = v_0$ and splits into two, the lifetime of the new branches is infinite. This is because the flow of mass between the two baby branches in Fig. 3.1 is always smaller than the free fall velocity, when the input of mass to each branch is v_0 .

In Appendix C I demonstrate that there exists a special value of the sum of body lengths

$$A_{\text{asy}} = \frac{l_1 - l_2}{l_1 + l_2} = \frac{v_1 - v_2}{[v_1 + (v_1 + v_2)]} \quad (2.7)$$

at which in the flow of mass between the two herring is balanced in such a way that the asymmetry ratio A_{asy} remains constant. In the vicinity of A_{asy} the bifurcation is a diverging branch of $[A - A_{\text{asy}}]$.

In the Appendix C I calculate the bifurcation of a new herring, averaged over all possible symmetries $-1 < A < 1$. The remarkable new result of this calculation is that there is a special critical velocity of the tip

$$v_c = v_{\text{asy}}/2 \quad (2.8)$$

at which the average bifurcation changes. If the velocity of the tip is less than v_c the average bifurcation of new herring is finite, if $v > v_c$ then this time it infinite. It means that consistently at velocities $v > v_c$ branching will lead to formation of stable new herring.

2.2.3 Critical Ratio

Suppose that there is a simple configuration of a large circular DNA (Fig. 2.2). The right part slowly overwinds the left part and small herring are created from time to time at the right tip of this structure. These small herring have symmetrical shape ($v_1 = v_2$) from the mass alone. Their longevity is controlled by the velocity of the tip $v = (v_1 + v_2)/2$. If $v < v_c$ they will disappear, if $v > v_c$

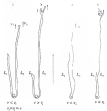


Figure 5.3. a), b) Critical ratio for a Y-shape configuration for a circular polymer. One branch is overweighing the other. When the ratio of the length of two branches $L_2 : L_1$ exceeds 2:1, the stable branching of the top becomes possible. c), d) For a linear polymer, the critical ratio is $L_2 : L_1 = 1:1$.

the small kernal will start to grow. The velocity v depends on the ratio of mass of the right and left parts of the DSA, L_1 and L_2 . Using Eq. 3.2.1 find that there is a ratio

$$L_1/L_2 = 1/3 \quad (3.9)$$

at which the velocity of the moving tip is critical. If this ratio is smaller than 1/3, then $v < v_c$ and all small kernal will disappear. As one part overgrows the other, the ratio L_1/L_2 grows with time. When the ratio becomes larger than 1/3, the velocity of the tip exceeds the critical velocity $v > v_c$. Small kernal created at the tip, become stable and start to grow. This critical ratio was clearly observed in my simulation of linear polymer.

3.2.4. Linear Polymer

The existence scheme presented in Appendix C can be easily modified for the case of a branching of a moving end of a linear polymer (see Fig. 3.3 (i) and (ii)). In this case I obtained for the critical velocity of a leading tip

$$v_c = \frac{2}{3}v_0 \quad (3.10)$$

The critical asymmetry ratio at which the branching of a leading tip will occur is

$$L_1/L_2 = 1/2 \quad (3.11)$$

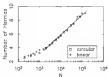


Figure 3.4: Average number of helices as a function of molecular size of the polymer. It shows logarithmic molecular size dependence for both circular and linear polymers (for $N > 1000$).

3.4 Statistical Results

3.4.1 Average Number of Helices

I have performed simulations in the size N range from 10^3 to 10^6 units (this corresponds to $10^2 \sim 10^5$ base pairs) for circular and linear polymers. I found very nice dependence of the average number of helices on molecular weight (see Fig. 3.4).

For large ($N > 1000$) I observed a logarithmic behavior of the average number of helices (see Fig. 3.4) for both linear and circular polymers. This confirms the theoretical prediction [6] of the statistical self-similarity of the melting polymer chain. This result is in qualitative agreement with the results of Dele and Vucelja

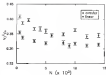


Figure 3.5: Average velocity of center of mass as a function of molecular size N . The velocity is independent of the molecular size of polymer up to possible topological restrictions. The average velocity of a linear chain is larger than that of a circular chain due to the end effect.

[86], who observed coiled structure in simulation of random loop chains ($N > 1000$). For shorter chains ($N < 1000$), the statistical self-similarity breaks down, and I do not observe two-like structure. The polymer spends most of its time in a simple configuration with only two branches.

3.4.2 Average Velocity

The results for the average velocity of a moving polymer at long times are shown in Fig. 3.4. For the circular polymer the average velocity approaches $0.03u_r$. For a linear polymer the average velocity is $0.04u_r$.

The result that the average polymer velocity is independent of the molecular weight is consistent with the model [43] and numerical simulations [86]. The very

slow decrease in the velocity can be explained by the logarithmic correction $\sim 1/\log N$ to the average velocity because the velocity is averaged over both non tree-like configurations and tree-like configurations.

3.4.3. Periodicity of the Motion of a Crawling Polymer

I find strong periodicity in the motion of circular DNA through the gel. The number of branches and velocity of the center of mass plotted as functions of time (Fig. 3.4 upper and lower graph respectively) show this periodic pattern. The average time of a cycle decreases linearly with the molecular weight of DNA (Fig. 3.5).

Successive interchanges between tree-like structure and Y-shape configurations take place regardless of molecular size. Y-shape configurations can be recognized as small plateaus with $n = 1$ on the upper graph and segments of exponentially growing velocity on the lower graph of Fig. 3.4.

The series of pictures in Fig. 3.6 shows a typical evolution picture within a cycle. The cycle starts with a Y-shape configuration with some asymmetry between left and right branches. This asymmetry increases slowly until the asymmetry ratio exceeds 3:1. At this moment the branching starts at the leading tip. The further evolution can be described in terms of a maximally well rounded tree like structure due to the competition between branches and the creation of new ones. If the two largest branches of the tree have comparable length (Fig. 3.6(a-c)) the branching at each of them slows down and smaller branches start to disappear. If, after the disappearance of smaller branches, the length ratio of two large branches remains less than 3:1, the sequence returns to the beginning of the cycle.

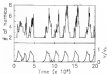


Figure 3.6 Number of kinks and center of mass velocity as a function of time for a circular polymer. The figure shows a periodic pattern. A large number of kinks are indicative of treelike structures. The plateau on the upper graph with $n = 2$ indicates a simple Y stage configuration. Only the kinks larger than $2a$ are counted. The velocity of the center of mass is $0.50a_0$ at the onset of the growth in kinks number (this corresponds to the critical linear velocity $u_c = 0.5a_0$).

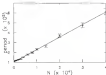


Figure 3.7 Dependence of the period on the molecular weight of the circular polymer. Our period is defined as the time between two consecutive major peaks in the velocity of the center of mass (see Fig. 3.4 and Fig. 3.8). The data are averaged over 100 periods.

(Fig.3-4[5]). The duration of each stage of the process is about the same and is proportional to the total length of the DNA. During the simulation, it is only possible to identify clearly stage I, (plateau in Fig.3.4). The boundary between stages II and III (increasing and decreasing velocity of center of mass) is often ill-defined.

The circular DNA stage is a simple Y-shape configuration about 50% of total time (see Fig.3-4). I observe similar behavior in the case of a linear chain. But the cycle for linear chains is not as regular as for circular chains. I explain this difference by the "free end effect" (see Fig.3.1). When the chain is in the unstable regime almost all of its branches are double folded. When two large branches of comparable length are formed, they are also often double folded. The folding



Figure 1.6: Time evolution of a circular polymer. The figure show a typical cycle between two consecutive Y shape configurations. The leading tip starts to branch as soon as the ratio of lengths of the two branches exceeds the critical ratio h_1 , h_2 . The tree is formed (c-d) and dies after formation of two major competing branches, or simplified again (e-f).

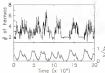


Figure 3.8: Number of kinks and center of mass velocity as a function of time for a linear polymer. The periodicity is much less clear, than on Fig. 3.4 due to less falling onto

low ends may create an asymmetry of the configurations, which is larger than the critical one, and the leading kinks start branching again. I found that due to the real effect a linear polymer stage in a sample N -stage configurations only 10% of the time (Fig 3.8)

3.5.4 The Splitting Probability and Size Distribution

Most of my computer simulations were done with the probability of tip splitting $p = 0.5$ [such that a tip reaches the distance of the previous tip has a 50% chance of splitting]. I checked the accuracy of my model in the choice of this parameter. In Fig 3.10 the kinks size distribution function $P(L)$ is plotted as a function of L on logarithmic scale for different splitting probabilities p ranging from 0.001 to 1. It clearly demonstrates the universality of the law $P(L) \sim 1/L^2$ (see Eq.

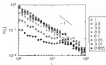


Figure 3.10: Size distributions of branches plotted for a bifunctional ($N = 1000$) dividing polymer at various up-splitting probabilities p . The straight line indicates $1/L$ dependence. At $p = 0.2$, the curves are indistinguishable.

a) for $p > 0.64$. If the probability of up-splitting becomes too low ($p < 0.64$), the distribution $P(L)$ is universal only for small size branches. The distribution resembles that of star chains, where configurations with two branches give the dominant contribution to the statistics of large branches with $L \sim N$.

On Fig 3.11 the frequency of branches of unit size $P(1)$ is shown for different up-splitting probabilities p ranging from 0.000 to 1. For the improvement of the accuracy, the frequency $P(1)$ is calculated as the average of curves shown in Fig 3.11 with the box $L = 1$. The slope $1/3$ in the double logarithmic plot suggests a following scaling behavior at constant L :

$$P(1) \sim p^{1/3}. \quad (3.12)$$

The frequency P increases and becomes constant at $p = 0.2$. I have no analytical

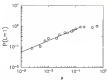


Figure 3.11: Values of the form-distribution function for unit size boxes, $P(L=1)$ as a function of top-creation probability p on logarithmic scale. The slope of this plot suggests a power law $P(L=1) \sim p^{0.5}$.

emphasis for the observed exponent $1/2$. I can combine the scaling laws Eq. 3.6 and Eq. 3.12 in a single phenomenological formula

$$P(L) \sim p^{1/2}/L \cdot f_1(N)p^{1/2} \quad (3.13)$$

where $f_1(x)$ is the cross-over function: $f_1(x) = x$ for small x and $f_1(x) = \text{const}$ for large x .

3.4 Summary and Discussion

I presented new analytical and numerical results for a simple deterministic model of magnetic DNA undergoing an strong gel electrophoretic field. The results can be summarized as follows:

(i) I confirm the obtained self-similarity of the shape of a moving polymer. The average number of kinks is proportional to the logarithm of the molecular weight (Eq. 3.5).

(ii) The average velocity is independent of molecular weight (with possible logarithmic corrections). It approaches 33% (34%) of the free falling velocity for a circular polymer (linear polymer).

(iii) I find the periodic evolution pattern similar to that observed by Dentch [40] in the motion of a circular polymer with a period proportional to its molecular weight. During a typical period the shape of polymer changes from a simple V-shape-configuration to a growing tree-like conformation and then to a decaying tree-like conformation. A circular[linear] polymer starts in the V-shape configuration about 33% (15%) of the time (which is truly remarkable). The previously

is much less pronounced for a linear chain due to a perturbative effect of free ends

(iv) In my simulations I observed the theoretically predicted threshold for branching $n_b = n_c/2$ and the critical mass 2.1 for a circular polymer

(v) The statistical properties of a moving polymer are almost independent of the probability p of tip splitting in the interval $0.5 < p < 1$ because of destructive interaction of numerous small branches or small nodes. At low $p < 0.5$ the branch size distribution scales with polymer size L and probability of tip splitting p (Eq. 4.12)

The main advantage of the deterministic model is its simplicity, which allows fast simulation of ultra-high molecular weight polymer. A possible drawback of the model is the absence of stored length. The effects of stored length are negligible for large polymers because of strong stretching during most of the cycle. But stored length can be important during the free fall regime. The effect of elastic forces during the free fall can change the free fall velocity of different parts of a polymer by a factor $1/N$, which might not be very important, but the accumulation of stored length during the free fall can result in a modified frequency of tip splitting [37]. I can agree that the increased frequency of tip splitting might not be impossible because of the stochastic effect, but this can only be checked by a future direct simulation of a more complicated model.

CHAPTER 4

CHARGED POLYMERS

Polyelectrolytes are polymers with ionizable groups [10-11]. When the polymer is in polar solvents, these groups are dissociated from the polymer and move away from the polymer. Therefore, the remaining polymer becomes charged. The dissociated ion groups are called 'counterions'. Polyelectrolyte systems are very common in nature and have numerous applications because they are soluble in water. Water is a bad solvent for many polymers. But if the molecules are charged, the monomers repel each other, therefore the polymer can't cluster in the water. Most biopolymers are polyelectrolytes. Well known examples are DNA, RNA and proteins. A large number of synthetic polyelectrolytes exist as well. Polysulfonic acid and polyacrylic acids are examples. They are used as super absorbers of water.

Polyelectrolyte solutions show a number of remarkable differences from that of neutral polymers from the basic properties like viscosity, osmotic pressure and light scattering pattern [12-17].

Because of their fundamental relevance to biology and biotechnology and due to their hydro-colloidal, polyelectrolytes have been of continuous interest in polymer science and a considerable theoretical work has been devoted to the various aspects of polyelectrolyte solutions [18-25]. Despite of this, the understanding on a polyelectrolyte solution still remains largely unsatisfactory.

The same theoretical difficulty arises with the long range nature of the Coulomb interactions. The distribution of charges introduces more than one length scale, which makes useful techniques for neutral polymers invalid for polyelectrolytes. The renormalization group theory or scaling theory are powerful techniques for the neutral polymer. In charged polymer systems it is difficult to apply them because of the long range nature of the Coulomb potential [3].

Polyelectrolyte solutions contain more than one component. The presence of counterions screens long range Coulomb interactions, which introduces another intermediate length scale. The complicated interplay between small and large scale interactions have a non trivial influence on the local structure of the polyelectrolyte chain. For example, the local chain structure influences the counterion condensation, and counterion condensation in turn modifies the long range interactions. The long range interaction is known to have a substantial contribution on the stiffness of the chain [30].

Due to these reasons, the charged polymers have been treated as an inhomogeneous problem because of the discrepancy between theoretical prediction and experimental results [30].

As an example of this controversy, there is a long standing debate regarding the "persistence length" [31-44, 56-59, 121], which is the local stiffness of a polymer chain. The persistence length is one of the important scaling parameters. The first scaling theory was provided by de Gennes et al [32]. In this model, it is assumed that the persistence length of the chain is proportional to the screening length, which is the interaction range of the electrostatic interaction between

the monomers. In another analytic approach by Delly and independently by Skolnick and Fixman[567] [81, 82], it was predicted that the persistence length is proportional to the square of the screening length. They calculated the energy required to bend a charged polymer and found that the stiffness of the chain is strongly enhanced by electrostatic interactions.

However, several computer simulations[84–86] indicate that the persistence length of a polyelectrolyte chain with counterions are much shorter than the GGE prediction. The perturbation of one surrounding the polyelectrolyte chain is much stronger than the Debye-Hückel estimation. Therefore, the screening of repulsive interactions between charges on the polymers by counterions is much stronger than the screening given by Debye-Hückel theory. In contrast to theory experiments clearly indicate that the persistence length is proportional to the screening length ($l_p \propto 1/\sqrt{\epsilon}$). As is discussed above, even after much theoretical work the origin of the stiffness of a charged polymer is not completely clear.

In spite of the relatively microscopic length scale, there has been progress in the study on macro-molecular properties of charged polymers [3–7, 181, 182].

In a good solvent, the portion of a polyelectrolyte is a series of stretch of electrostatic blobs [82] (see Fig. 4.1). Inside of each electrostatic blob, the Coulomb repulsion is not sufficient to deform the chain.

In a poor solvent, the chain collapses in the form of a compact globule [1, 183]. The polymer chain has negative second virial coefficient which corresponds to effective attractions between the monomers. The overall shape of a charged polymer in a poor solvent is determined by a balance of Coulomb repulsion and



Figure 4.1. Various conformations of a polyelectrolyte chain depending on the solvent quality: a) A polyelectrolyte chain in a good solvent. b) An elongated globule of polyelectrolyte in a poor solvent. c) A necklace of globules in a poor solvent.

surface tension. One can control the net charge by changing the pH [106]. If the polymer is charged, the Coulomb repulsion changes the globular shape of the polymer. The total energy of the polymer can be lowered either by a deformation in the form of an elongated globule [106–108] or by splitting into two smaller globules connected by coiled strings [9–7].

The cylindrical deformation was suggested by Klechkov [109]. The size of the cylinder is obtained by minimizing the sum of the surface energy and Coulomb energy at fixed volume. There is no variability in the cylindrical globule which is similar to the variability of a charged liquid droplet [106–108]. Kantor and Kardar [6,7] proposed that the polymer (a polyelectrolyte) with short range attractions and long range repulsion will form a necklace of compact globules connected by coiled strings (Fig. 4.1 c). This idea is extended by Dobrynin

et al. [5] to polyelectrolytes in a poor solvent. I study the conformation of a ring polyelectrolyte in the following chapter. In addition to the authors the information with respect to the change of the net charge, the ring polymer has a glassy phase and lyotropic effects.

CHAPTER 3

MULTIPLE CONFORMATIONS IN POLYAMPHOLITES

The stability of a weakly charged polyelectrolyte with respect to formation of a solution of globules was recently pointed out by Kantor and Kardar [8,7]. I related these results from a linear to a ring polymer. There is now interest in a ring polymer - the competition between linear and ring-coil-like formation. This is analyzed theoretically using mean field theory and experimentally verified. There are lyotropic effects in the shape of the chains. If the total charge is increased the linearly extended coil-like ones are dynamically more preferable. When the charge is decreased, the covalent shapes are preferable. I remark on the probable connection to the multiple phase transitions observed in polyelectrolyte gels.

3.1. Cascade of Transitions in a Linear Polymer

Polyampholytes (PA) are charged polymers which have positive and negative charges distributed randomly along their backbone [106]. The strength of electrostatic interaction and the relative ratio of positive and negative charges depend on the dielectric constant and the pH of the solvent. The interplay of long range electrostatic interaction and short range forces of other origin may produce sharp structural transitions upon changing certain properties of the solvent [111-123]. The interest in the properties of PA have been caused not only by their rich

structural properties, but also by the obvious relevance to the protein folding problem [112-114].

The overall shape of a randomly charged linear polyelectrolyte chain depends on the magnitude of the net charge Q of the molecule [8, 7]. If this charge is less than the critical one Q_c , the molecule has the shape of a compact globule, where mutually attractive positively and negatively charged groups closely compensate each other. The globule has spherical shape in order to minimize its external surface. When the net charge exceeds the critical value $Q_c \sim \kappa^2 R$, the globule splits into two. The new configuration has larger surface area, but the separation of two resulting globules reduces the energy of electrostatic repulsion. This splitting is analogous to the classical instability of a charged droplet described by F. L. Ingli [105]. Because both smaller globules are made of the single polymer chain, they can not be too far apart from each other and remain connected with a string. As larger charges each globule can again split, therefore forming a loose chain of globules, connected strings. The number of globules is controlled by the net charge Q . The optimal number of globules is approximately [8, 7]

$$n \sim \frac{3\pi}{4} Q^2 / Q_c^2 \quad (8.1)$$

where Q_c is Haythigh charge ($Q_c = 4\pi\epsilon_0 R^2 \kappa$ - surface tension, R - radius of the globule).

The nonuniformity in the distribution of charges along the chain results in fluctuations of the charge at each globule. These fluctuations ($\sim N_0^{1/2}$ where N_0 is the number of monomers in a globule) are of the order of Q_0 for a globule

Therefore, the fluctuations caused by the crosslinks are always important in the size distribution of globules. There is another factor which affects the statistics of the size distribution of globules. For the globules on a linear chain, the effects of disordered sequences are strongest in the middle of the chain, and weakest near the chain ends. As a result, the size of globules and the distance between them depend on the position of these globules on the chain. The combined effects of crosslinks and position dependence make any analytical and numerical study of the globule distribution in the linear configurations very difficult [5-7].

3.2 Ring Polymers

In this work I considered the configurational properties of circular chains. There are two motivations. First, a ring has an additional symmetry compared to the linear chain, since all sequences have the same structural environments in the rest of the chain. The effects of different ring topologies discussed above can be elucidated. This allows the study of the asymptotic size distribution of globules in smaller chains than in the linear case. Second, the physics of chain entanglements of the circular polymers might provide an insight into the chain phase separation in polyelectrolyte networks [96]. In first approximation, these networks can be thought of a collection of cross-linked polyelectrolyte rings. In the same way as different parts of the ring can be mutually attractive, different chains inside the elementary cell of a polyelectrolyte network can be attractive and form a secondary network of compact globules connected with single or double strings.

7.3 Mean-Field Calculations

First, I will neglect effects caused by disorder and assume that the distribution of charges along the various chains is almost homogeneous. The total charge of any fragment of a polymer of length n is nQ_0/N . This is similar to the case of a homogeneously-charged polyelectrolyte (in a bad solvent [8]), where the monomers are attracted to each other due to short range interactions, but repelled due to long range electrostatic interactions. The only difference to [8] is the circular form of the chain. The configuration of a polymer is controlled by the overall charge. If this charge is small, the polymer is in a compact globular configuration, if the charge is large, it should be in an extended multi-globule configuration. There are two major possibilities. One possibility is that the extended configuration is linear similar to the configurations of a linear chain (see Fig. 5.1 $a \rightarrow b \rightarrow c$). Another possibility is that the multi-globule configurations will have a complex tortuous shape as shown in the Fig. 5.1 $a \rightarrow b \rightarrow c$. The difference in the energy of these configurations depends on the microscopic details of the model.

Consider the energy of the three globule configurations of a linear and a circular polymer (see Fig. 5.1 c and c'). There are three major contributions to the energy of these configurations: The surface energy of the globules, the surface energy of strings and the Debye-Hückel energy of the microcharges between the globules. The surface energies of globules of both configurations are about the same and I compare only the two remaining contributions:

$$E_{\text{linear}} = \frac{3}{2} \frac{(Q_0/N)^2}{R} + 3n_0 R \quad E_{\text{circular}} = 3 \frac{(Q_0/N)^2}{R} + 3n_0 R \quad (1.2)$$

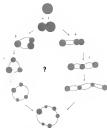


Figure 1-1: Illustration of the transition of a ring polymer. When the change of the polymer becomes, new configurations can be listed following trace of circular sequences. If mechanism is present, there is a mixture of linear and circular patterns.

Here $Q_0/3$ is the charge of the globules, R is the distance between them, v_0 (v_1) is the linear tension of a double (single) string. The tension is the energy needed to pull a unit segment of the string out of the globule. Minimizing both energies with respect to R I find

$$R_{linear} = 2\pi\sqrt{3}Q_0/v_0, \quad R_{circular} = 6Q_0/v_1. \quad (3.3)$$

If the double folded string tension v_1 satisfies the following inequality,

$$v_1 > 3/2v_0, \quad (3.4)$$

the circular configuration has lower energy compared to the linear configuration. If the reverse inequality holds, the linear configuration is dominant. The ratio (3.4) is special to the three globule configuration. If the number of globules n is large ($n \gg 1$), the energies of linear and circular configurations are

$$E_{linear} = \frac{(3Q_0/v_0)^2}{R} n \cdot \text{Log}(n) + (n-1)v_0 R, \quad E_{circular} = \frac{(3Q_0/v_1)^2}{R} n \cdot \text{Log}(n) + nv_1. \quad (3.5)$$

In this case, I have the inequality $v_1 > v_0$ as the condition of lower energy of the circular configuration. As n increases, the energy difference ΔE between linear and circular configurations converges to $v(n)Q_0^2$ where $v(n)$ is a function of the number of globules and v_1, v_0

$$v(n) = 2\sqrt{3}v_1 - v_0^2 Q_0^2 (\text{Log}(n))^{1/2}. \quad (3.6)$$

I expect that the maximum energy needed to pull out a double folded string is about twice the energy needed to pull a single string: $\sigma_2 \approx 2\sigma_1$, the actual ratio depends on the details of the short range interactions of monomers on the two strings. If the monomers are interacting through screening forces (weak form of δ -bond), it might happen that the work energy of the double string σ_2 can be even less than that of a single string σ_1 .

However, for charges $Q > Q_0$, the maximum energy configuration can be linear or circular, depending on the details of the model. The most likely scenario is that, with small number of globule n the preferable configuration is linear, while for large n it is circular. In the limit case when the electrostatic repulsion between monomers dominates over all other interactions, the maximum energy configuration is always an open ring.

4.4 Effect of a Random Charge Distribution Phase Diagram

Randomness in the charge distribution creates a fluctuation of the net charge in each globule. Consider n globule configurations. The typical charge fluctuation in each globule is $\sim q_0/Nq^{1/2}$. The fluctuation in electrostatic energy per globule with radius $r \sim [N/q]^{1/3}a$ is of the order of $\delta E_{\text{fluct}} \sim q_0^2/2[N/q]^{1/3}$. If the energy δE_{fluct} is comparable to the difference between the energy per globule in linear or circular configurations $\delta E/n \equiv (E_{\text{linear}} - E_{\text{circular}})/n$, the effects of randomness will completely control the final arrangement of globules. Setting

$\partial E_{\text{free}}/\partial n$ equal to $\partial E/\partial n$. I have

$$\alpha(n)Q_0^2(n) \approx Q_0^2(n)(N/n)^{1/3} \quad (5.7)$$

where $n \equiv Q_0^2/N$. The equation represents a line in the phase diagram plotted in coordinates Q_0^2/Q_0^2 ($= n$) and N . In the $n \gg 1$ limit

$$N \approx \alpha(n)^3 Q_0^2/Q_0^2 \quad (5.8)$$

with $\alpha(n)$ given by Eq. 5.4. The Eq. 5.8 provides an upper bound for the region in the phase diagram where the effects of randomness are dominant (Fig. 5-6). Above this line (region II) the minimum energy configuration is either n -cluster or linear depending on the microscopic details of the model. The dashed vertical line in the region I of the phase diagram separates regions with different optimal numbers of globules, n . In this region there are also numerous meta-stable configurations of various shapes. The energy difference between the different topological configurations is of the order $\sim \partial E/\partial n$. Below the line given by Eq. 5.7 (eq. on II) the ground state energy configurations are completely random. In addition, there are many meta-stable states with similar energies. The lower bound of region I is given by the equation

$$Q_0 = c_0 N \quad (5.9)$$

Here c_0 is a model dependent constant. Below this line (region III) the charge on the chain is so large that the only stable configurations are open rings (see Fig. 5-6).

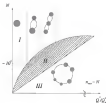


Figure 3.3 Phase diagram of a diatomic polymer. In regions I and II meta-stable states are observed. In region I the ground state is either linear or circular depending on the model. In region II the ground state is controlled by fluctuations. In region III (strong net charge limit $Q > c_0 N$), only open ring configurations are observed.

3.5 Metastable Configurations and Energy Barriers

In regions I and II of the phase diagram there are many configurations which do not have the lowest energy but are relatively stable. Some of them can be relatively easy transformed into another (soft mode). The simplest way to obtain a slightly different configuration is to make cyclic shift of the chain between each pair of nearest globules by one or two monomers. This transformation preserves the topology of the overall structure of globules connected by strings. The difference in energy of the new configuration is of the order of $\sim q_0(Q_0/a_0)/a$. There are about H such states for each topologically distinct configuration. Another type of transformation is related to a change in topology. The typical barrier between two such configurations can be estimated from the energy needed to bring two globules together and then, regrouping them (see Fig. 3.1). This energy is of order $E_0 \sim (Q_0^2/a_0^2)/a/(Q_0/a_0)^{1/2}$. An estimate of the number of configurations with different topology can be made by evaluating the number K of connected clusters made from n globules. This is the well known "isotactic" problem [20], and the number of configurations is $K \sim n^k e^{kn}$, where the exponent $k = 5/2$ for three dimensions and k is a constant of the order of one.

3.6 Symmetry

If the overall shape of the chain is increased (due to changes in solvent properties), the formation of linear structures is more preferable. Consider the transition from two to three globules. This transition might occur by splitting one of the globules with formation of circular or linear three globule configuration or three

in Fig. 3.1 c and d'. Because of the electrostatic repulsion between the $+$ and $-$ globules, the splitting of the globule in parallel direction is dynamically more preferable (Fig. 3.1 c $\rightarrow$ d') than the splitting in perpendicular direction (Fig. 3.1 c $\rightarrow$ b').

The linear configurations formed in this way may not be the ground state. However, they are meta-stable and dynamically preferable. The time required to overcome the energy barrier between linear and circular configurations is proportional to $e^{U^{\ddagger}/kT}$. Depending on the temperature and the size of the globules, the transition from one topology to another cannot be observed during reasonable time.

In the reverse situation, when the total charge decreases from a large value, the formation of a circular configuration is dynamically more preferable.

3.2 Monte-Carlo Simulation

My model and the details of the Monte-Carlo simulation are very similar to that of Kantor and Karim [3, 4] for a linear chain. I consider a ring polymer as a flexible chain of N randomly charged monomers. Each monomer has charge $+q_0$ with probability p and charge $-q_0$ with probability $1 - p$ independent of all the others. A typical random sequence of N monomers has a total monomer charge of about $(2p - 1)q_0$. I characterize the sample system by chain length N , temperature T and net charge Q . At a given net charge several quenched configurations are tested. The interaction between a monomer pair i, j is the electrostatic interaction $U_{i,j} = q_i q_j / r_{i,j}$. During the simulation the monomers

are placed on a cubic lattice. Each site can be occupied by only one monomer, and the length of the link between two subsequent monomers was allowed to vary from 1 to 4 lattice units. The Monte Carlo simulation creates new configurations by attempting to move each monomer in a randomly oriented direction. The new configuration is accepted with probability $e^{-\Delta E/kT}$, where ΔE is the energy difference between the old and new configurations.

I ran the simulation in the temperature range $0.1 \sim 1$ measured in $q^2/2k_B$ units and chain size N from 16 to 128. Most of the simulations were done at temperature $T = 0.1$, with $N = 64$. The temperature is chosen in such a way that the system arrives at the equilibrium state in a reasonable MC time, but low enough to see clear quantum patterns.

The peak transition patterns are defined for the various models. For example, the more I increase the maximum allowed distance between the subsequent monomers, the more linear configurations will be preferable.

I found a very rich configurational diversity. This is caused by the random nature of the charge distribution. In a linear polymer, the randomness in the charge distribution contributes only to the size distribution of the globules. In a ring polymer, there are additional possibilities to combine two remote parts of the chain containing complementary charged monomers. The transitions have different patterns for various polymer sizes. As a rule, the effect of randomness on configurations and transitions with the same number of globules is more pronounced for small N . For $N < 10^3$ the transition of splitting one globule was highly irregular for different sequences, but for $N \geq 10^3$ the transition occurs at



Figure 5.5: Different meta-stable configurations out of the same chain with fixed random charge distribution.

$Q = Q_0 = q\sqrt{N}$ as predicted by mean field theory. For the maximum length $N = 128$, the 3-globule to 5-globule transition was affected by randomness in the charge distribution (see phase diagram Fig. 5.2). If I increase the excess charge at fixed N , the number of globules increases. In this case each globule contains less monomers and I found very irregular cluster shapes. Some sample configurations are shown in Fig. 5.5. For each particular charge distribution, different meta-stable configurations can be accessed by repetition of the cooling and heating procedure described below. The easiest way to distinguish different configurations is by direct observation. It is very difficult to assign any quantitative parameters for the different configurations.

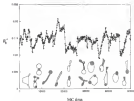


Figure 3.4 Plot of R_2^2 vs. Monte Carlo time. In the beginning of each cycle for the first 10% steps the temperature is increased to $T = 18$. Then the system is at $T = 0.1$ for the rest of the cycle. R_2^2 has plateaus at various levels indicating different conformational configurations shown below the graph.

In the Fig. 3.4 I plot the 4th moment of the polymer size $\langle r^4 R_g^2 \rangle$ vs $\frac{1}{2} \ln \Sigma_{\text{eff}}(n) = n_2/2$ while the system undergoes the heating and cooling cycles. In the beginning of each interval (1/3 of the interval), the system is heated to $T = 0.5$ and configurations become nearly Gaussian. $\langle r^4 R_g^2 \rangle$ goes down for these configurations. Then I drop the temperature to $T = 0.1$ to ensure the relaxation to the local energy minimum. One can distinguish the configurations by the value of R_g^2 . There are large scale-plateaus which include small scale fluctuations.

The linear stretched configuration has the largest R_g^2 (shown as the highest plateau), the circular open shape has smaller R_g^2 (middle plateau). The configurations with a large collapsed part or a Gaussian configuration has the smallest value of R_g^2 . After each heating and cooling process, I reach a different configuration and a different level-of-plateau. The large scale jumps imply the change from a circular to a linear configuration or vice versa. The small fluctuations are due to the shift in monomer level. With chain length $N = 64$, the longest relaxation time I observe to reach to the local minimum is of order $N^3 \approx 262144 \sim 4000$ time units.

Upon increasing the net charge $\langle Q_1^2 \rangle > Q_0$, I observe a ring configuration with different sizes of globules as a dominant configuration. I define Q_1 as the maximum net charge which allows exclusively ring configurations. Q_1 is proportional to the polymer size N . $Q_1 = c_1 N$. The model dependent constant c_1 is approximately 0.7 in my model.

1.4 Discussion

I found that ring polyanaphtholates have remarkable non configurational properties as a result of competition between tendencies to form linear or circular structures. The different parts of a ring may be situated at such angles forming a compact globule, so that the configuration has the form of a random cluster of such globules. There are many different non-stable configurations of this type for the same chain and their energies are about equal. I find the region of the phase diagram where the effects of randomness in the distribution of charges along the chain are most important. I suggest that similar multiple conformational phenomena might be observed in a polyanaphtholite gel. In the same way as different parts of a circular chain attract, producing various configurations, the different parts of the strands inside a gel can attract. Local rearrangement of such configurations may involve strands from adjacent elementary cells and may be thermodynamically unstable. I expect that under the change of the external conditions (temperature, pH, salt concentration, etc.) the rearrangement will happen in abrupt steps which could involve the whole sample. Nevertheless, my attempt to link the multi-level volume phase transition observed in polyanaphtholite gels [111] using the analogy with single chain phenomena should be considered with caution. In my approach I neglected the possibility of screening effects due to the presence of counterions, free of salt and other polyanaphtholite molecules. Future development should incorporate these effects of screened interactions as well as the thermodynamical contributions of other ions.

CHAPTER 4 CONDENSATION THEORY ON COUNTERIONS

In this chapter, I study the condensation theory of counterions. In a polyelectrolyte, polyelectrolytes dissociate into charged monomers and counterions. When the polyelectrolyte chain is strongly charged, the electrostatic potential near the chain is huge and some of the counterions remain bound. This phenomenon is known as “counterion condensation” or “Manning condensation” [4]. The ion condensation is important even in a very dilute solution because in the very vicinity of the chain, the electrostatic energy of counterions (measured in $k_B T$ unit) can always be larger than unity. Treating counterion condensation analytically is difficult because it occurs in the regime of strong Coulomb interaction where the Debye-Hückel (DH) approximation is not valid.

First I review the well known solution of the nonlinear Poisson-Boltzmann (PB) equation in a 2-D cylindrical cell geometry [155]. Then I present a new solution of the PB equation with different boundary conditions appropriate for the isolated polyelectrolyte chain. This will provide a simple explanation of a critical charge which is $1/3$ lower than in Manning’s theory. Finally I will discuss how the interactions between two test charges in the monomer region are modified due to the presence of counterions. This result is then related to the local structure (stiffness) of the polyelectrolyte chain.

3.1 Manning Condensation Theory

I consider the electric field produced by a long rod like charged polymer in the presence of counterions. The rod consists of N monomers with radius a and every i th monomer carries unit charge e . The charge parameter λ is

$$\lambda = l_B/a, \quad (3.1)$$

where $l_B = e^2/\epsilon_0\epsilon_r k_B T$ is the Debye length which is a parameter describing the strength of electrostatic interactions. For typical polyelectrolytes, the Debye length is about 7 Å in water.

If I ignore the contribution of counterions, the electrostatic potential satisfies Laplace equation. The solution is obtained by Gauss theorem as $\Phi(r) = -2\lambda \ln(r/a)/\lambda_B$. The counterion density around the chain is given by Boltzmann statistics as $n_c(r) = n_0 \exp\{-\Phi\} = r^{-2\lambda}$. The total number of counter ions per unit length within a distance r from the chain is

$$H(r) = \int_a^r 2\pi n_c r' dr' \quad (3.2)$$

When the line charge density λ is larger than one, the above integral diverges in the vicinity of polymer indicating the strong condensation of counterions on the charged rod. As the condensation proceeds, the counterion clouds effectively reduce the strength of Coulombic interactions. The effective value of the charge seen far from the rod is lower than the nominal charge density on the polymer. The condensation stops when the effective line charge density is equal to unity.

This simple condensation theory by Manning [8] describes the condensation as a transition between two states: the bound state and the free state, which means the effective charge is unity for large charge density. Manning's theory shows fair agreement with many experiments. However, it is oversimplified picture [155–158].

In a more accurate approach, the electrostatic potential of the polyelectrolyte chain in the presence of counterions should be described by the PB equation. (The potential is measured in unit of $k_B T / \epsilon$)

$$\nabla^2 \Phi(\rho) = -4\pi l_B \sum_j n_j(\rho) \quad (3.3)$$

where $n_j = n_j(\rho, \dots)$ is the concentration of the positive [negative] ions. The concentration is determined by Boltzmann statistics $n_j(\rho) = n_j \exp(-\beta \Phi(\rho))$. Therefore, I have

$$\nabla^2 \Phi = 4\pi l_B^2 / \lambda_D^2 [\rho_+ \exp(\beta \Phi) + \rho_- \exp(-\beta \Phi)] \quad (3.4)$$

If the potential is small, the PB equation can be linearized, resulting in the Debye-Hückel equation. The effective potential produced by a single charge is then given by

$$\Phi_{\text{DH}} = l_B \frac{q}{\rho} \exp(-\kappa \rho) \quad (3.5)$$

The contributions from different charges can be added algebraically. The screen length κ^{-1} is related to the Debye length and concentrations by the following equation

$$\kappa^2 = 4\pi l_B \sum_j n_j \quad (3.6)$$

However, in the vicinity of the charged polymer, one can always find a region where the electrostatic potential is large, $\Phi \gg 1$, even for a very dilute solution. In this region, the nonlinear aspect of PB equations becomes important. Thus the correct confinement theory should include the aspect of our hierarchy. In some special cases, it is possible to solve the nonlinear PB equations exactly [336].

6.2 Review of the 3-D Cell Model

Swain et al. have studied the interaction between the polyelectrolyte chains and counterions using the PB equation [130–134]. They assume that the polymer are infinite rods with cylinder radius a and are all parallel to each other. In between these rods, there must be equipotential surfaces where the electric field vanishes ($\mu = R_0$).

Each chain with its surrounding counterions is independent of all the other chains. Therefore the problem is to solve the electrostatic problem of single rigid cylinder with counterions in a 3-D cylindrical cell [136]. The electrostatic potential in this cell satisfies the following Poisson-Boltzmann equation

$$\nabla^2 \Phi = -\alpha^2 \exp\{-\Phi\} \quad (6.7)$$

with the boundary condition

$$r \frac{\partial \Phi}{\partial r} \Big|_{r=a} = 0 \quad (6.8)$$

$$\frac{1}{2} r \frac{\partial \Phi}{\partial r} \Big|_{r=R_0} = -1 \quad (6.9)$$



Figure 3.1. The geometry of the cell model. The electric field is fixed at the boundary. The polymer is approximated as an infinite rod with cylinder radius a . The center of each rod is located at the center of each cell. The net charge within each cell vanishes due to the electroneutral boundary condition.

Note that Papanicolaou's solution is controlled by two parameters: the charge density on the rod λ and the cell size R_0 .

The two solutions below and above Manning condensation are, respectively,

$$\Phi_1 = \log \left[\frac{R^2 \rho^2}{2\beta^2} \sinh^2(\cosh^{-1} \beta + \beta \log(\frac{R}{R_0})) \right], \quad \lambda < 1 \quad (3.10)$$

$$\Phi_1 = \log \left[\frac{R^2 \rho^2}{2\beta^2} \sinh^2(\cosh^{-1} \beta + \beta \log(\frac{R}{R_0})) \right], \quad \lambda > 1 \quad (3.11)$$

where β is related to the line charge density parameter λ by the following relation:

$$\lambda = \frac{1 - \beta^2}{1 - \beta^2 \tanh^2(\beta \log(a/R_0))}, \quad \lambda < 1 \quad (3.12)$$

$$\lambda = \frac{1 - \beta^2}{1 - \beta^2 \tanh^2(\beta \log(a/R_0))}, \quad \lambda > 1 \quad (3.13)$$

The distribution of counterions can be calculated using Boltzmann statistics from the potential (3.38) and (3.11)

These relations indicate that there is no bound state in the distribution of counterions. However, one can divide space into two regions: 1) an inner region in the vicinity of the chain where the energy is larger than $k_B T$, therefore counterions are considered as bound, and 2) an outer region where the interaction is smaller than $k_B T$, therefore the counterions are moving freely. The surface potential $\Phi(r) = \psi_0$, ψ_0 is the value of the cylindrical well; increases almost linearly with the increase of the line charge density λ until λ reaches unity. For large line charge density $\lambda \gg 1$, $\Phi(r = \kappa) = \psi_0$ increases logarithmically.

It was shown that when $0 \leq \lambda \leq 1$ the effective charge density increases to unity as the condensation proceeds. On the other hand, if $\lambda \gg 1$ the effective charge density is limited by $1/\lambda$ [60]. In the infinite well model (in the limit $R_0 \rightarrow \infty$) [34], Flory also showed that the charge density is limited by unity when the spacing between the charges is the Debyeon length.

4.2 New Solution of the Poisson-Boltzmann's Equation

In this section, I present a new solution which satisfies different boundary conditions. I will show that this new solution describes a different physical situation. I consider a dilute solution of polyelectrolytes where polyelectrolyte chains are isolated from each other. In this limit, one can still use cylindrical coordinates near the charged rod. But as a distance comparable to the chain length (the 1-D boundary condition must be considered). The 1-D solution in the vicinity of the



Figure 8.1 The polyelectrolyte chain in a chain solution. The electric field does not vanish at the boundary.

cylinder does not need to satisfy the charge neutrality condition at the cylindrical boundary shown in Fig. 8.1.

I use cylindrical coordinates ρ, ϕ, z in the vicinity of the charged rod-like polymer (all lengths are measured in terms of the cylinder radius a). The potential inside of the cylinder is described by the PB equation ($\nabla^2\Phi = -q$). In the vicinity of the cylinder ($\rho < \rho_0 < a$), the potential is large ($\Phi \gg 1$), and only the first term of the r.h.s. of Eq. 8.4 is important, therefore,

$$\nabla^2\Phi_1 = -4\pi\epsilon_0\epsilon\kappa^2\Phi_1 \quad (8.14)$$

where index "1" indicates that the solution is valid inside of the cylindrical region ($\rho < \rho_0 < a$). In the vicinity of the charged rod, the effect of finite length of the polymer is negligible. I found the solutions of this equation for the infinite length

rod has the very simple form

$$\Phi(\rho) = \log\left(\frac{G}{\rho^2 - \frac{1}{4}\rho_0^2}\right) \quad (8.12)$$

The solution has two tuning parameters λ and G . There is a simple relation between λ and the charge density on the surface

$$\lambda = -\frac{1}{2} \frac{d\Phi}{d\rho} \Big|_{\rho=1} = \left(\frac{2}{1-\lambda}\right) + \frac{1}{2} \quad \lambda = 1 - \frac{1}{2}(1-\frac{1}{2}) \quad (8.13)$$

The parameter λ gives the location of the hypothetical surface inside of the charged cylinder where the potential diverges. The asymptotic behavior of the electrostatic potential ($\rho \rightarrow \infty$) is $\Phi \sim 2 \log(1/\rho)$. The effective charge density seen from the outside of the cylinder is universal value $\lambda_{\infty} = 3/2$. The counterion density in the solvent ($\rho > 1$) is given by

$$n_{+} = \nabla^2 \Phi = \frac{2}{(\rho - \frac{1}{4})^2} \quad (8.14)$$

The total number of counterions in the distance ρ from the rod can be calculated by integrating the above equation Eq. 8.14 $n_{+}(\rho) = \int_1^{\rho} n_{+}(\rho) 2\pi \rho d\rho$. The main contribution to this integral comes from the region near the charged rod. The relation Eq. 8.13 is valid only for strongly charged polymers with charge $\lambda \geq 1/2$. When the charge density $2 \leq 1/2$, the PB equation can be linearized and the solution has the form $-\lambda \log(\rho)$. The contribution of counterions is negligible in this linear solution limit.

8.4 3-D Extension

The constant C in Φ_1 will be determined by the mixed boundary conditions which relate the inside solution Φ_1 to the solution Φ_2 outside of the boundary. I consider another hypothetical cylinder characterized by the radius ρ_1 and length d surrounding the charged rod. For the outside of this cylinder ($r > \rho_1$, $|z| > d/2$) the potential is expected to be small ($\Phi \ll 1$). In this region, the constant density (Eq. 8.17) is very small so that I can consider the Laplace equation of a charged rod with constant line charge density $2/\pi$. The electrostatic potential in this region can be obtained by calculating that of a charged cylindrical rod with radius ρ_1 and length d . Therefore, the electrostatic potential is

$$\Phi_2 = \frac{2}{\pi} \sum_{n=0}^{\infty} \left(\frac{r_0}{r_1} \right)^{2n+1} P_n(\cos \theta) \quad (8.18)$$

where $r_0(r_1)$ is the smaller (larger) of $d/2$ and r .

I match the boundary conditions in the 3-D geometry at a finite distance from the center of the rod. Therefore, my new solution describes the region where there is no overlap between the chains. The picture of counterion condensation in 3-D is different from the 2-D cell model. Since the condensation has to be brought from 3-D space rather than 2-D, the entropic loss of a counterion in 3-D is of the order of $-\pi \log(\rho_1)$ instead of $2 \log(\rho_1)$ in 2-D. In Manning theory the condensation occurs in the cylindrical cell geometry when the electrostatic energy gain of bringing the counterion to the surface $2 \log \rho$ becomes comparable with the 2D entropic loss of the counterion. My result describes condensation as a

dilute solutions of polyelectrolytes. In this case the maximum should be brought from the λD region and the energy has a $\lambda \log \rho$ which is $1/2$ times larger than in Manning's case. Therefore, the onset of condensation occurs at higher charge density.

If the end effects are not neglected, the constant C' has a dependence. The electrostatic potential at the edge diverges logarithmically

$$\psi(r=a, z) = \lambda \log\left(\frac{a^2 - z^2}{2}\right) + \frac{2\lambda}{\epsilon} z^2 \quad (8.18)$$

where $\rho = \frac{2}{a^2 - z^2}$

8.5 Interactions between Test Charges

I will show that due to the enhanced concentration of ions near the chain the actual interaction is different from Debye-Hückel type interaction. Consider a small test charge on the charged cylinder. Due to the presence of the test charge there is a small perturbation in the potential proportional to the change of charge density. The perturbed electrostatic potential can be written as a sum of the non-perturbed potential and small perturbations $\psi = \psi_0 + \psi_1$. The PB equation for ψ_1 can be written as

$$\nabla^2 \psi_1 = \frac{n^2}{2} \exp(\psi_0) \psi_1 \quad (8.19)$$

The interaction of charges near the chain are controlled by two non-classic static scales. One of them is the size of the necklace region λ_c near the chain

where the Debye-Hückel approximation is not valid. Another scale is the "local" Debye screening length R_D^l near the chain. By comparison with Eq. (8.1) we define the local Debye length by

$$R_D^l = (\kappa^2 / \text{diag}(\Phi_{ss}))^{-1/2} \quad (8.12)$$

where Φ_{ss} is the non-perturbed potential. Therefore the interaction between two test charges must be modified by using the local Debye length. If the distance r between two test charges is less than R_D^l the interaction between them is not screened.

By taking the derivative of Eq. (8.1), I obtain the change of the potential due to the small perturbation in charge density

$$\delta\Phi = \delta\Phi_D = \delta\Phi_0/r \quad (8.13)$$

This relation shows that the screening of counterions reduces the interaction strength by factor of $1/\lambda$. Suppose one of the charges is on the chain and another is placed at a distance r ($r > R_D^l$) away in perpendicular direction. The field line starting at the charge on the cylinder can reach the other charge with a probability $1/r$. Due to the counterion condensation, the strength of the field lines is reduced by an additional factor $1/r$ given by Eq. (8.13). Therefore, the interaction decays as $1/r^2$. If the second charge is placed on the cylinder, the field lines passing near the cylinder have high chance to go to the other charge. Two test charges on the cylinder are interacting through field lines draining through

the outer region ($r > R_0$). The interaction will be reduced by an additional factor of $1/r$, leading to an overall decay of $1/r^3$.

I confirmed this argument by a numerical path integral method. In a computer simulation, the random walk starting from a point on the cylinder in the electrostatic field $\Phi(z)$ has a probability $1/r^2$ to go to the other point at a distance r along the perpendicular direction. The probability is $1/r^3$ if the second point is at a distance r on the cylinder. If the distance between the charges is larger than μ , the interaction is described by the Debye-Hückel formula.

CHAPTER 7

PERSISTENCE LENGTH OF A POLYELECTROLYTE CHAIN

I present a first principles calculation for the persistence length of a linear chain in both the strongly and weakly charged case. In the presence of salt ions using curved cylindrical coordinates we calculate the change in the electrostatic potential and ion concentration in the vicinity of a bent chain. I find the persistence length to dependence on the Debye length as $l_p \sim \kappa^{-1}$ for a strongly charged polymer. This result can be explained by enhanced screening effects due to the high concentration of ions in the vicinity of the chain, compared to the concentration in the bulk. For a weakly charged polymer, we recover the DGF result $l_p \sim \kappa^{-2}$ [31,42].

7.1. Persistence Length

The difficulty in treating charged polymer lies in the non-trivial influence of the long range Coulomb interaction on the local structure of polymer. The persistence length l_p is the parameter describing the flexibility of the polymer chain [3,4]. The persistence length is defined as the decay length of the correlation length of the tangential vector. The persistence length can be extracted from the measurement of various physical quantities [36–38]. Many theoretical works have attempted to calculate the persistence length of a charged polymer [31–34, 43–45, 47]. Under the presence of electrostatic interactions, the bending length can

remote part of the chain closer to each other, therefore, the total electrostatic energy increases. That energy change is proportional to the persistence length and the square of the curvature κ :

$$\Delta E = \frac{1}{2} l_p \kappa^2 l_B T \quad (7.1)$$

The classical theory by Odijk [11] and independently by Skolnick and Fixman [52] (OSF) for a rigid rod like polyelectrolyte assumes that the polymer rigidity becomes greatly enhanced by the electrostatic repulsion of its monomers. The persistence length l_p of a charged chain with bare persistence length l_b and charge density f can be written as the sum of the bare persistence length l_b and electrostatic contribution l_{elst} , $l_p = l_b + l_{elst}$ with

$$l_{elst} = l_b \kappa^{-1} f^2/4 \quad (7.2)$$

where l_b is Kuhn's length. In OSF theory, the interaction between two charges on the polymer is described by Debye-Hückel potential

$$V(r) = kT l_B / r \exp(-\kappa r) \quad (7.3)$$

where κ is the inverse of interaction range R_D , Debye radius, and is related to the total ionic concentration c_0 in the solution, $\kappa^2 = 4\pi l_B c_0$. In their original calculation, OSF estimated that the persistence length of the polyelectrolyte is proportional to κ^{-2} , which is much larger than the effective interaction range κ^{-1} . The OSF theory shows reasonable agreement for an extremely stiff chain, which

has large bare persistence length. However, for intrinsically flexible polyenes, analysis, however shows strong deviations from GSE theory. As we decrease the ion concentration c , the persistence length increases as c^{-1} . Using the variational method, Baroni and Jansup [88] argued that for intrinsically flexible chains, the fluctuations in chain configuration can have substantial influence on the rigidity of the chain. Therefore, the persistence length increases of the order of the electrostatic screening length. This result is consistent with the picture of an electrostatic blob suggested by de Gennes et al (see Fig 4.1.4). Inside of the electrostatic blob the thermal energy is comparable to the Coulomb interaction so that the chain remains undistorted by electrostatic interaction. However, the calculations by Lu and Watson [89] show that the effect of conformational fluctuations of a flexible ring polymer does not change the GSE result.

On the other hand, several computer simulations indicate that the picture holds by the extension is much stronger than indicated by the GSE formula [94-97]. This implies stronger screening of the electrostatic interactions and shorter persistence length. More recent molecular-dynamics simulations by Mylon and Kremer [98-99] show that the persistence length has a strong dependence on its screening length ($l_p \sim \kappa^{-1}$, $p < 1$).

7.2 Debye-Hückel Approximation

It is clear that there are limitations in applying GSE theory to a polymer system. The Debye-Hückel potential is obtained as a solution of a screened

version of the Poisson - Boltzmann equation

$$\nabla^2\Phi = -\kappa^2\Phi \quad (7.4)$$

In the actual problem, in the vicinity of the chain the potential Φ is larger than $k_B T/\epsilon$ and the PB equation becomes nonlinear. Therefore in the vicinity of the chain the concentration of ions is higher than in the bulk. The screening effects should be enhanced. Le Dou [\[33\]](#) and Forman [\[34\]](#) have calculated the persistence length numerically using the nonlinear Poisson-Boltzmann equation rather than the linearized Debye-Hückel approximation. The numerical value of the persistence length shows strong deviation from the GSF result at high ionic concentrations [\[34\]](#).

In the following sections I discuss the relevance of the nonlinearity of the PB equation in the vicinity of the chain. I extended the analytic approach to obtain analytic expressions for the case over from $\sim n^{-1/2}$ (rigid chain) to $\sim n^{-1/3}$ (flexible chain) behavior of the persistence length. I perform a straightforward calculation of the distribution of the potential and the ion concentration in the vicinity of a slightly bent charged polymer chain with curvature radius R . Then, I calculate the bending energy by expanding the PB equation up to the second order of $1/R$ in curved cylindrical coordinates. This expansion procedure is similar to Forman's approach as described in [\[34\]](#). It appears that the main distribution in the vicinity comes from the region of radius $r < R$, near the chain

3.1. Nonlinear Solution in Cylindrical Coordinates

In this section, I study the nonlinear PB equation numerically in cylindrical geometry in order to illustrate the nonlinear effects of the PB-equation. I consider a dielectrically charged rod with radius a with free charge density λ . With Eq. 6.4, I write

$$\nabla^2 \Phi = \frac{d^2}{dr^2} \sinh(\Phi) \quad (7.5)$$

with the boundary conditions

$$\frac{1}{r} \Phi \frac{\partial \Phi}{\partial r} \Big|_{r=a} = -\lambda \quad (7.6)$$

$$\Phi(r)_{r=0} = 0 \quad (7.7)$$

Following the ideas of the previous chapter, I confirmed that the solution of the nonlinear PB equation has following properties: 1) When $\lambda \leq 1$ the solution is analytic everywhere. 2) When $\lambda \geq 1$ the solution has singular surface inside of the cylinder at the distance $r = b$ from the cylinder center. The parameter b has also weak λ^{-1} dependence. 3) The location of the singular surface b is related to $\lambda^{-1/2}$ via the following equation

$$b(\lambda^{-1/2}) - b(\lambda^{-1/4}) = \alpha b^2 / \lambda^{-1/4} \quad (7.8)$$

There is a difference to the coil model where the solution is controlled by two independent parameter λ and R_0 . I point out that the solution of the one-loop Poisson-Boltzmann equation is controlled by only one parameter: $b(\lambda^{-1/2})$. 3) If

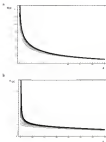


Figure 7: (a) The solution of the PB equation for $\lambda = 1, 2, 3, 4$, increasing from the lower to the upper. Fig. (b) The concentration distribution as a function of distance from the cylinder for various values of λ . The concentration decreases dramatically in the vicinity of cylinder. The concentration density in the region away from the cylinder is not affected by the charge density change.

$\delta/\alpha^2 \ll 1$, the solution of the nonlinear PB equation has universal properties. Far away from the rod, the solutions with different λ are on top of each other. As λ increases the solutions are emerging to a universal curve [see graph 7.1]. The two graphs 7.1 a) and b) show the constant density and potential distribution for various values of surface charge density. The influence of large λ can be seen only near the cylinder. The potential near the cylinder is much larger than δ_0/ϵ and counterion density is strongly enhanced in this regime. The change of the insulator potential and counterion density upon the change of the surface charge density is negligible at a distance. As predicted by other theoretical approaches, we can clearly see that the redistribution of counterions compensates the excess charges.

7.1. Calculation of the Binding Energy

In order to obtain the persistence length, I follow Flory's expansion method [34] using the curved cylindrical coordinates with radius of curvature R . The geometry of curved cylindrical coordinates is shown on the Fig 7.2. The PB equation in the curved cylindrical coordinates can be written in the following form

$$\frac{1}{\rho(1 - \rho \cos \theta) \frac{\partial}{\partial \rho}} \rho(1 - \rho \cos \theta) \frac{\partial}{\partial \rho} \Phi + \frac{1}{\rho(1 - \rho \cos \theta) \frac{\partial}{\partial \theta}} \frac{1}{\rho(1 - \rho \cos \theta)} \frac{\partial}{\partial \theta} \Phi = \text{const} \exp(\Phi - \chi) \quad (7.9)$$

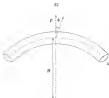


Figure 7.3 The geometry of curved cylindrical coordinates are shown. The curvature α is the inverse of the radius R .

The electrostatic potential is expanded with respect to the inverse of the radius of curvature $\alpha = 1/R$

$$\Phi(\rho) = \sum_{l=0}^{\infty} \Phi_{lm}(\rho) \cos(m\theta) \alpha^l \quad (7.36)$$

Here the electrostatic potential Φ is measured in terms of $4\pi\epsilon_0^2/\epsilon$. All lengths will be measured in terms of the radius of cylinder a . Assuming that the bending curvature is very small $\alpha \ll 1$, we expand Φ up to the second order of α and neglect the higher order of α

$$\Phi_L(\rho) = \Phi_{L0}(\rho) + \Phi_{L2}(\rho) \cos 2\theta + (\Phi_{L1}(\rho) + \Phi_{L3}(\rho) \cos 2\theta) \alpha^2 \quad (7.37)$$

The electrostatic contribution to the persistence length is obtained from the energy change

$$\Delta E = \frac{q\ell_D^2}{2} \Delta E_1 / \ell_D T \quad (7.13)$$

The total electrostatic energy of the ion system in a given state is the work required to raise its charge density from zero to its final value λ . The electrostatic energy increase per unit length due to the bending can be obtained by the electrostatic energy difference between the straight (Φ) and bent (Φ') cylinders

$$\Delta E = e \int d\Omega \int_0^L (\Phi'_{\text{bent}} - \Phi_{\text{straight}}) d\lambda \quad (7.14)$$

where $\int d\Omega$ is the integration over the azimuthal angle. After angle integration all odd functions will vanish. Therefore, the electrostatic contribution to the persistence length comes from the second order term. The energy of bending is

$$\Delta E_1 / \ell_D T = e \int d\Omega \int_0^L (\Phi_{20}^{\text{bent}} + \frac{1}{2} \Phi_{11}^{\text{bent}}) d\lambda \quad (7.15)$$

To first order of $\kappa \cos \theta$ we have

$$-\frac{\partial \Phi_0}{\partial r} + \frac{1}{r} \frac{\partial \Phi_{11}}{\partial r} + \frac{\partial^2 \Phi_{11}}{\partial r^2} + \frac{1}{r^2} \frac{\partial \Phi_1}{\partial \theta} - \kappa^2 r^2 \Phi_{11} = 0 \quad (7.16)$$

The solution of Eq. 7.16 Φ_{11} is almost independent of λ in a distance far from the rod (approximate universality). To second order in κ , I consider all noncompensated Φ_2 terms

$$\Delta_2 \Phi_2 + \frac{\partial^2 \Phi_{20}}{\partial r^2} + \frac{1}{r} \frac{\partial \Phi_{20}}{\partial r} - \frac{\kappa^2}{2} r^2 \Phi_{20} = 0, \quad (7.17)$$

where the source term $S(\phi)$ is given by

$$S(\phi) = -\frac{\rho}{2} \frac{\partial \Phi_0}{\partial \phi} - \frac{1}{2} \frac{\partial \Phi_0}{\partial \phi} - \frac{\Phi_0}{\lambda} - \frac{\rho^2}{2} \Phi_0^2. \quad (7.17)$$

First, let us consider a weakly charged polyelectrolyte ($\lambda < 1$). The last term of Eq. 7.16 is negligible because there is no convection contribution, therefore the screening by the counterions is weak. I assume that there is no significant charge redistribution upon binding, this leads the radial function $\Phi_{\text{eq}}(r_{\text{eq}}) = 0$. The source term $S(\phi)$ is approximately ~ 1 . Therefore Eq. 7.16 can be approximated by

$$\frac{\partial^2 \Phi_{\text{eq}}}{\partial r^2} + \frac{1}{r} \frac{\partial \Phi_{\text{eq}}}{\partial r} = -\lambda. \quad (7.18)$$

The last term of Eq. 7.16 becomes important when $\Phi_{\text{eq}} \approx 1/\rho^2 \lambda$. This means that the amplitude of Φ_{eq} should reach at the screening length $\rho \approx \lambda^{-1}$. By integrating Eq. 7.18, we obtain the surface potential $\Phi_{\text{eq}}(r=1) \approx \lambda r^{-1}$. In order to obtain the persistence length, we then integrate with respect to λ , $\int_0^{\lambda^*} \Phi_{\text{eq}} d\lambda$. I recover the ODF result for weakly charged polymer

$$l_p \approx \lambda^2 \kappa^{-1}. \quad (7.19)$$

For the strongly charged polyelectrolyte ($\lambda > 1$), the interaction range κ^{-1} is replaced by the local Debye radius $(\kappa^*)^{-1}$, which is defined by Eq. 4.20. The interaction range $(\kappa^*)^{-1}$ is drastically reduced by the increased concentration of counter ions near the cylinder where the electrostatic potential is large ($\Phi \approx 1/\rho < (\kappa^*)^{-1}$). I can see that there are two physically different regions: in the

last regime (the very vicinity of the cylinder), the PB equation consists of two dominant contributions

$$\Phi_{zz}'' + \frac{\Phi_z'}{\rho} = \frac{\rho^2}{\ell} e^{\Phi} \Phi_{zz} = 0 \quad \Phi_{zz}'|_{\rho=1} = 1 \quad (7.22)$$

The second term $(e^{\Phi})^2 = \frac{\ell^2}{\rho^2} e^{2\Phi} \Phi_{zz}$ is present only in the very vicinity of the cylinder $\rho \ll (\alpha\ell)^{-1}$. As a result of the integration, we have

$$\Phi_{zz} = \ell \int_1^{\rho} \frac{\rho'^2}{\rho'} e^{2\Phi} d\rho' \Phi_{zz} = (\lambda - 1) \Phi_{zz} \quad (7.23)$$

where we use the identity $\int_1^{\rho} \frac{\rho'^2}{\rho'} e^{2\Phi} d\rho' = (\lambda - 1)$. Outside of this regime, the situation is same as in the weakly charged case. As in the case of blocking conditions, the charge density λ is replaced by unity

$$\frac{d^2 \Phi}{d\rho^2} + \frac{\Phi \Phi'}{\rho^2} = -1 \quad (7.24)$$

Same as in the weakly charged polymer, Φ_{zz} is of the order of unity at $\rho = \alpha^{-1}$.

Suppose we approach the charged cylinder from the distant. The electrostatic potential is increasing monotonically until $\rho = (\lambda - 1) \Phi_{zz}$. As we get closer to the cylinder, the screening term becomes important so that the magnitude of the potential starts decreasing. I can replace $\frac{\ell^2}{\rho^2} e^{2\Phi} \Phi_{zz}$ by a constant and solve the differential equation. In the weakly charged case, the potential should be of the order of unity at $\rho = 1$. Therefore, we find the value of Φ_{zz} on the cylindrical surface

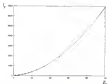


Figure 7.5: Perimeter length vs. Delay length as given by Eq. 7.33 with $\lambda = 4$. The data points are taken from Foxman's numerical calculations.

In order to obtain the perimeter length for the strongly oblate rod ($\lambda > 1$), we have to integrate Φ_{10}^* and Φ_{10}^* for the $0 \leq X' \leq 1$ and $1 \leq X' \leq \lambda$ regions respectively. The perimeter length is the linear combination of the two integrals we obtain following formula

$$L_p = \pi a^{1/2} + 4a^{1/2} \log(\lambda + 1). \quad (7.35)$$

To fit the perimeter a, b by the comparison with Foxman's numerical results for two different λ . I obtain $a = 0.034$ and $b = 7.33$ which allow the best fitting for both of λ . The result shows good agreement with Foxman's numerical calculation (see Fig. 7.5). By analyzing the formula Eq. 7.33, I find that the crossover

arises when the screening length is approximately $\kappa^{-1} \sim 1\text{fm}$. For a small salt concentration $\kappa^{-1} \gg 1\text{fm}$, the second term of the Eq. 7.33 is dominant. At a large salt concentration $\kappa^{-1} \ll 1\text{fm}$ and the persistence length shows a linear dependence on κ^{-1} .

Summarizing: using a qualitative analysis of the perturbation expansion in curved cylindrical coordinates, we obtained a simple phenomenological formula which describes the crossover of the persistence length from the weakly to the strongly charged limit.

CHAPTER 8 CONCLUSIONS

In this thesis I studied the conformational properties of polymers. I first discussed two polymer systems in which the conformational properties are intimately related to the dynamic properties. In the problem of a polymer chain penetrating a membrane I calculated the probabilities of different configurations of the polymer and the corresponding mobilities. I found the optimal configuration which gives the main contribution to the transport through the membrane in both Rouse and Zimm dynamics. This process of diffusion through the membrane can be used for separation of polymers with different lengths. I showed that the total permeability has a power law dependence on the molecular weight.

I also studied the random motion of DNA molecules undergoing gel electrophoresis. In a strong electric field, the configuration of DNA consists of many growing and shrinking branches. The power law behavior of the branch size distribution confirms the hypothesis of a self similar tree-like structure. It is observed that DNA has a periodic evolution pattern and stays in a couple "Y"-shaped configurations during a considerable fraction of the period. Although the mobility of DNA is independent of molecular weight in constant field electrophoresis the knowledge of the configurations at a given time will help to develop more sophisticated methods of electrophoretic separation of DNA.

In the second part of the thesis I studied the conformational properties of charged polymers. I considered a single charged polymer which is isolated from other polymers.

I showed that a polyelectrolyte chain has a glassy phase where the configurations are controlled by the repulsion or the charge distribution along the chain. The metastable configurations in this phase are a result of the competition between the tendency to form linear or circular structures. I suggested that some of multiple conformational phenomena could occur in polyelectrolyte gels, which could be connected to the sol-gel phase transitions observed in the experiment by Tanaka [11]. By solving the Poisson-Boltzmann equation, I investigated the phenomena of osmotic condensation and the resulting stiffness of a polymer. The flexibility of a strongly charged polyelectrolyte can be explained by the strong screening of the Coulomb's repulsion due to the attached counterion concentration near the polymer. I also described a new condensation scenario for the dilute solution in which the critical change in $1/T$ is much larger than in the classical Maassig theory.

The understanding of the conformational picture of a single polymer is the first step towards a study of melts or polymer solutions in equilibrium or nonequilibrium regime, which is essential for many practical purposes. Many properties of polycondensates/solutions are nonuniversal. Much more work is needed to reach a level of understanding equivalent to that obtained for neutral polymers. In a polymer solution, interchain interactions must be well in equilibrium situation. The study of many chain effects including entanglement effects will be the subject of future

study. In addition to the analytical approach, the importance of numerical studies is obvious. The numerical simulation can include corrections explicitly which goes beyond the Debye-Hückel or Poisson-Boltzmann approximation.

APPENDIX A PROOF OF EQUATION 3.1

In the absence of excluded volume interactions the relation $\rho_{\text{ex}} = \frac{1}{2}\rho_{\text{eq}}$ can be reached by the following simple gedanken experiment. Let us assume that the same polymer concentration is established on both sides of the membrane, but the polymers on one side are slightly different from polymers on the other side of the membrane (e.g. they can be deuterated). The polymers of both types start to diffuse and mix each other. The total concentration of both types of polymers will be the same as in equilibrium, but the concentration profile of each component can be calculated only if the dynamics of the polymer mix is known. In the middle of the membrane the concentrations of each component should be equal to each other because of the symmetry of the problem. The sum of the two concentrations, i.e. the total concentration, should be the same as in equilibrium. This means that the concentration of each component is equal to one half of the equilibrium concentration as stated in Eq. 3.1.

APPENDIX B CALCULATION OF PARTITION FUNCTION

When the polymer crosses the membrane, it must penetrate the membrane at least once. I calculate the partition function $Z_1(\mu, N_1)$ ($Z_2(\mu, N_2)$) of a polymer of length N_1 (N_2) attached to the membrane. Then I write the partition function of the whole polymer $Z(\mu, N)$ as a product of two partition functions:

$$Z(\mu, N) = Z_1(\mu, N_1) Z_2(\mu, N_2) e^{-\beta} \quad (\text{B } 1)$$

One may set $N_1 = N_2 = N/2$ in which case the constraint from the membrane is maximal. The weight $e^{-\beta}$ is attributed to the single membrane crossing.

From the well known solution of the first passage problem [10], I calculate the Green function of random walk of length n which starts at the surface of a membrane and does not cross the membrane again. One also needs the Green function of a walk which starts and ends on the membrane and does not have any other contacts with membrane in between. I call these Green functions G_1 and G_2 , respectively (see Fig. B 1 a and b)

$$G_1(x) = \sqrt{\frac{2}{\pi n}}, \quad G_2(x) = \frac{1}{2n} \sqrt{\frac{2}{\pi n}} e^{-x^2/n} \quad (\text{B } 2)$$

The configurations contributing to the partition function $Z_2(\mu, N_2)$ are shown in Fig. B 1 c. Similar configurations were studied for the electrolyte problem [20-22]



Figure B.1. (a) b) Graphical representations of the functions G_+ , G_- . c) Diagrammatic series of all contributions to $D(p, v)$

The statistical weight of each of them can be written as a multiple product of G_+ and G_-

$$D(p, N_0) = \sum_{k_1, k_2} v^{k_1+k_2} \int G_+(n_1) G_-(n_2) \dots G_-(n_{k_2}) R(N_0) = \sum_{k_1, k_2} n_1^{k_1} v^{k_1+k_2} n_2^{k_2} \dots n_{k_2}^{k_2} \quad (\text{B.3})$$

When $k_1 = k_2 = 0$, the polymer passes the crossbar only once. The total number of crossings is $k_1 + k_2 + 1$. In terms of $D(p, N_0)$, $D(p, N_0) < 1/v$ $\Leftrightarrow$ $v < 1/(k_1 + k_2 + 1)$ is given by

$$v < 1/k \Leftrightarrow \int_{n_1, n_2} n_1^{k_1} v^{k_1+k_2} D(p, n_1) D(p, n_2) D(p, N_0)_{n_1, n_2} \quad (\text{B.4})$$

Let us define the Laplace transform $\tilde{D}_1(p, v)$ of the one-side partition function. The evaluation of the partition function $\tilde{D}_1(p, v)$ can be made by means of a diagram technique (see Fig. B.1 c). The Laplace transforms of $G_+(p, v)$, $G_-(p, v)$

we

$$\tilde{G}_0(\mu, s) = \sqrt{\frac{\pi}{s}}, \quad \tilde{G}_0(\mu, s) = e^{-s/\lambda} \quad (B.3)$$

Therefore, I have in the large n limit ($\mu \rightarrow k_0/n \ll 1$)

$$\tilde{G}_0(\mu, s) = \frac{\tilde{G}_0(\mu, s)}{1 - \tilde{G}_0(\mu, s)\lambda} \approx \frac{\sqrt{\pi\lambda} + \sqrt{s}}{\sqrt{s}(1 - \lambda)} \quad (B.4)$$

Here $\lambda = e^{-\mu}$. After the inverse Laplace transformation, I find

$$G_0(\mu, N/\lambda) = \text{Exp}(\mu^2 N/\lambda) \mathcal{E}r f \left(\sqrt{\frac{\pi N}{\lambda}} \right) \quad (B.5)$$

Combining Eq. B.1 and Eq. B.5, I obtain the partition function $Z(\mu, N)$ as shown in Eq. 3.1 in chapter 3. In order to calculate the relative weight of the configurations with k overlaps, I have to perform the inverse Laplace transform of $Z(\mu)$. Since $Z(\mu)$ behaves like $1/\mu^2$, the relative weight of configurations with k overlaps is $\sim k/N$.

APPENDIX C CALCULATION OF THE CRITICAL VELOCITY

Here I describe the evolution of two small horizons until the disappearance of one of them. I calculate the average lifetime τ of a horizon from its birth until its disappearance and average it over all possible asymmetries $-1 < A < 1$.

I consider the equation of motion for two horizons with length L_1 and L_2 (Fig. 3.3). I assume stable mass input into each segment with corresponding rates $\dot{L}_1$ and $\dot{L}_2$ (the dimensionless variables $\dot{L}_i = v_{\text{eff}}/\dot{L}_i$). The total length of both horizons is $L_0 = L_1 + L_2$ and the change of L_0 is proportional to the total input $\dot{L}_0 = \dot{L}_1 + \dot{L}_2$

$$dL_0/dt = \dot{L}_0 v_0 \quad (C.1)$$

If the value is independent of time, $\dot{L}_0 = \text{constant}$, then $L_0(t) = L_{00}(t) + v_0 t$, where $v_0 = L_{00}/\tau = \dot{L}_0/\dot{L}_0$.

The equation of motion for the asymmetry factor $A = (L_1 - L_2)/L_0 = L_1/L_0 - 1/2$ can be obtained from Eqs. 3.1 and 3.3

$$\frac{dA}{dt} = \dot{A}_0/L_0 + (\dot{L}_1 L_1 - \dot{L}_2 L_2)/L_0^2 = \frac{1-L_1}{L_0} \frac{4+(1-A)(1-L_1)}{1+v_0} \quad (C.2)$$

where the value difference is defined as $\dot{L}_0 = \dot{L}_1 - \dot{L}_2$. This equation can be integrated directly

$$A + \frac{1}{1-L_0} = \left(A_0 + \frac{1}{1-L_0} \right) \left(\frac{1+v_0}{v_0} \right)^t \quad (C.3)$$

3.6

where the exponent $\varepsilon = L_2(T) - L_0$ and A_0 is the initial value of the asymmetry. The Eq. (3.4) can be solved for the time t it takes to reach an asymmetry factor A :

$$t = -t_0 + t_0 \left(\frac{A + L_2(T) - L_0}{\sqrt{A_0 + L_2(T) - L_0}} \right)^2 \quad (3.6)$$

When one of the terms disappears it means that either $L_2 = 0$ or $L_2 = 1$. For definiteness I assume that the second term disappears, so at this moment the asymmetry $A = 1$. Eq. (3.6) with $A = 1$ gives the lifetime for this process as a function of initial asymmetry A_0 . I find the average lifetime by averaging 1 over all values of initial asymmetry A_0 :

$$\frac{1}{t_0} + 1 = \int dA_0 \left(\frac{1 + L_2(T) - L_0}{\sqrt{A_0 + L_2(T) - L_0}} \right)^2 \quad (3.7)$$

(Note that the integrand is divergent in the vicinity of $A_0 = -L_2(T) - L_0$. But $x \in [L_0, 1]$ the integration over this singularity is convergent, as the lifetime Γ is finite.) It means that the newly formed fermion disappears after some finite time. On the other hand, if $x \geq 3(L_0 > 1)$ the integral is divergent, which means that the newly formed fermion are statistically stable (as long as the system stays confined and the growing fermion do not attempt to split). The critical velocity is obtained when $x = 1$ with symmetric input, $L_1 = L_2 = 1/2$. This results in the critical velocity $v_c = v_{th}/2$.

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